SOME STUDIES OF MOLECULAR COMPLEXES OF INTERHALOGEN COMPOUNDS

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W. Keith Meyer

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This is to certify that the

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SOME STUDIES OF MOLECULAR COMPLEXES
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W. Keith Meyer

has been accepted towards fulfillment
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Major professor

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By

W. Keith Meyer

A THESIS

Submitted to the School for Advanced Graduate Studies of Michigan
State University of Agriculture and Applied Science
in partial fulfillment of the requirements
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AN ABSTRACT

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ABSTRACT

A series of new molecular complexes has been prepared. Complexes of iodine pentafluoride with pyridine, 2-methylpyridine, dioxane, 2-fluoropyridine, and trifluoroacetic anhydride have been made. Complexes of IBr, ICl and ICl_3 with dioxane and a variety of substituted pyridine derivatives have been made. Melting points, molecular formulae and qualitative observations of the colors and stabilities of most of the complexes have been tabulated.

The electric moments of 3-chloropyridine, 2-fluoropyridine, 3-fluoropyridine and 2,6-dimethylpyridine have been measured in benzene solution at 25° C. The electric moments of seventeen molecular complexes of organic amines and ethers with interhalogen compounds have been measured at 25° C. in solution in a nonpolar solvent. The results were interpreted in terms of a model in which a lone pair of electrons of the nitrogen or oxygen atom is donated to the iodine atom of the interhalogen compound. The dative bond so formed is polar in character and the percent charge transfer was calculated for each complex from the difference between the observed moment and the moment calculated for no interaction. The dative bond was assumed to be linear with the axis of the interhalogen compound and the plane of the pyridine ring except in the case of iodine pentafluoride where it was assumed to be at an angle of 30° to the axis of the tetragonal pyramidal molecule.

Partial phase diagrams were completed for the systems pyridine-iodine pentafluoride and dioxane-iodine pentafluoride. There is evidence of 1:1 compound formation in both systems and, in addition, of a 1:2 compound in the dioxane-iodine pentafluoride system. From the ultra violet absorption spectra of a series of solutions of the complexes in carbon tetrachloride the dissociation constants of five of the complexes were obtained.

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INTRODUCTION

Molecular complexes of organic amines and ethers with the halogen and interhalogen compounds have been intensively studied in recent years. However, only a single halogen fluoride complex, dioxane-iodine pentafluoride, has been reported. Since the physical and chemical properties of halogen fluoride complexes with ethers and amines should be of interest as they might provide a new class of mild fluorinating agents, the preparation and study of a variety of such complexes was undertaken. In addition an investigation of a variety of new complexes containing ICl, IBr and ICl_3 similar to the iodine pentafluoride complexes was undertaken.

The stability of complexes of this type may be established by measuring dissociation constants spectrophotometrically. Information concerning the nature of the dative bond between the two molecules of the complex may be obtained by measurement of the electric moment. A study of the electric moments of a series of molecular complexes was therefore undertaken with dissociation constants also being measured in several cases.

The temperature-composition diagram for the condensed phases of a system such as ICl.pyridine shows the number of compounds formed, their composition, approximate stabilities and their melting points. In several cases a study of the phase diagram was undertaken to provide this information.

HISTORICAL SUMMARY

One of the classical reviews of complexes up to the time of its publication in 1927 was Pfeiffers (38) book, Organische Molekülverbindugen. In 1954 Andrews (1) published a review article on aromatic molecular complexes[1] limited to complexes of the "donor-acceptor" type. Work on molecular complexes of halogens and interhalogens with nitrogen and oxygen-containing compounds will be reviewed here. Molecular complexes are formed by the interaction of compounds in which there is a sharing of electrons between the components, resulting in a semblance of a chemical bond. One of the components donates electrons while the other acts as an electron acceptor. These interactions are weak as evidenced by their low heats of formation (18, 27, 29, 52) in the order of a few kilocalories per mole as compared to normal chemical bonds with heats of formation in the order of tens of kilocalories per mole. For this reason these substances are called complexes rather than compounds.

A great deal of research has been done on complexes of iodine with pyridine. Chatlet (6) reported the isolation of the 2:1 pyridine-iodine complex as yellow transparent crystals which quickly decomposed to iodine and pyridine. He also

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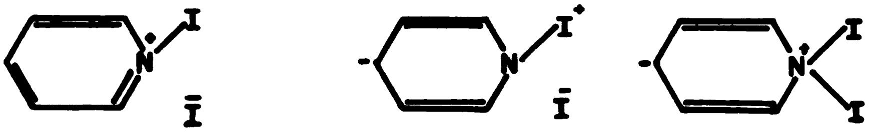
[1] The terms molecular complex, addition complex, molecular compound and molecular addition compound are often used with substances of this type. The author will use the first term for description of these products.

reported isolation of two hydrated complexes with the compositions[1] $I_2 \cdot Py(H_2O)_6$ and $I_2 \cdot Py_4(H_2O)_{24}$ (7). The dipole moment of the anhydrous pyridine-iodine complex has been reported as 4.5 D. in cyclohexane (30) and 4.17 D. in benzene (59). The latter value is probably in error since iodine forms a weak molecular complex with the solvent itself.

Mulliken (36) suggested possible structures for the pyridine-iodine complex

and Syrkin and Anisimova (59) proposed similar structures



to explain the high dipole moment of the $Py \cdot I_2$ complex. The work of Hassel (19-22) on complexes of oxygen and nitrogen-containing compounds with interhalogen compounds indicates that some of these proposed structures probably don't exist. He has shown that the pyridine-iodine monochloride complex is planar with the N-I-Cl group linear and that in the dioxane-iodine monochloride complex the O-I-Cl arrangement is linear.

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[1] The symbols Py and BPy will be used for pyridine and bipyridine respectively in formulae.

From thermal analysis Fialkov (14) found two compounds in the pyridine-iodine monochloride system having mole ratios of 1:1 and 1:2 respectively. In solution in polar solvents the complexes dissociate to give $Py.I^+$ and ICl_2^- ions. Popov (39) has shown that both pyridine and 2,2'-bipyridine complexes with iodine monochloride dissociate in acetonitrile to form the ICl_2^- ion and Py_2I^+ and $BPyI^+$ ions respectively. He was unsuccessful in attempting to prepare the Py.2ICl complex.

The dipole moment of the pyridine-iodine monochloride complex has been measured in benzene and found to be 8.20 D. (26). This value seems a little high in comparison to the electric moment of the pyridine-iodine complex.

Williams (67) succeeded in isolating the pyridine-chlorine and the pyridine-bromine complexes, which have melting points of 47° C. and 62° C., respectively. The chlorine complex decomposes spontaneously in air.

Popov and Rygg (40) studied, by spectrophotometric methods, the molecular complexes of pyridine, 2-methylpyridine and 2,6-dimethylpyridine with iodine, iodine monochloride and iodine bromide. They calculated equilibrium constants for the dissociation of the complexes into their components in carbon tetrachloride solution at 25° C. These dissociation constants are listed in Table 1.

TABLE 1

EQUILIBRIUM CONSTANTS OF AMINE-INTERHALOGEN COMPLEXES IN CARBON TETRACHLORIDE

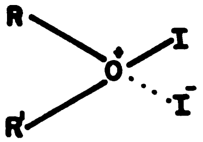
Complex	Equil. Const.
Pyridine. ICl	2.07×10^{-6}
2-Methylpyridine.ICl.	1.12×10^{-6}
2,6-Dimethylpyridine.ICl. . .	1.12×10^{-5}
Pyridine.IBr.	7.73×10^{-5}
2-Methylpyridine.IBr.	4.25×10^{-5}
2,6-Dimethylpyridine.IBr. . .	2.67×10^{-4}
Pyridine.I_2	9.88×10^{-3}
2-Methylpyridine.I_2	6.68×10^{-3}
2,6-Dimethylpyridine.I_2 . . .	1.97×10^{-2}

Besides the complexes listed above, the only other organic complex reported with iodine bromide is the one with dioxane (44, 54).

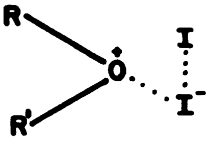
A slightly different approach to the problem of determining whether there is interaction between halogens and the solvent is by use of infrared spectra (37). Iodine monochloride has a fundamental absorption band at 375 cm.$^{-1}$ in carbon tetrachloride. Shifts of this stretching vibration frequency to longer wavelengths are observed as the iodine monochloride complexes with the donor. This band is shifted to 270 cm.$^{-1}$ for the strongest complex, pyridine-iodine monochloride. The intensity of the absorption also increases as the vibration frequency shifts to smaller wave numbers.

Molecular complexes of halogens and interhalogens with oxygen-containing compounds have been mainly limited to ethers and alcohols. Lilich and Presnikova (32) determined the stability constants of dioxane and methanol complexes of iodine, bromine, iodine monochloride and iodine bromide in carbon tetrachloride solutions. Keefer and Andrews (28) also determined equilibrium constants of complexes of iodine and bromine with some aliphatic alcohols and ethers.

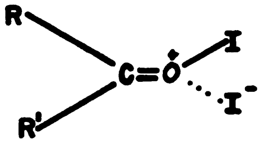
Mulliken (35) postulated the following structures for iodine-ether complexes



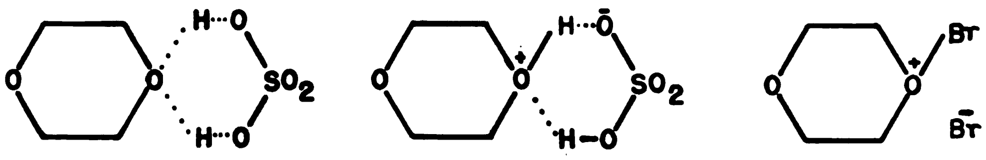
and



where the iodine axis is perpendicular to the R-O-R plane. He proposed that the iodine-ketone complexes resonated between two structures of this type



where the axis of the iodine molecule is coplanar with the ketone skeleton. Similarly, Syrkin (59) proposed structures of the type



for dioxane complexes with iodine, bromine and sulfuric acid. These structures were postulated to account for the dipole moments, which are 0.95 D., 1.30 D., and 4.65 D., respectively, in dioxane. In the light of Hassel's work on crystal structures (19) some revision of these structures is necessary. He has shown that halogen and interhalogen complexes with ethers, thioethers and amines are linear with respect to the plane of the molecule and the halogen axis. Similarly in the dioxane-bromine complex, the O-Br-Br arrangement is also linear and the O-Br bond is not in the plane formed by the oxygen atom and its two adjacent carbon atoms. Kortüm and Walz (31) reported the value 3.00 D. for the dipole moment of the dioxane-iodine complex in cyclohexane solution. Fairbrother (13a) reported the value 1.3 D. for the dipole moment of the dioxane-iodine complex in dioxane solution.

Rheinboldt and Boy (44) give the melting point of the 1:1 dioxane-iodine monochloride complex as 56-8° C., while Hassel gives 103° C. as the melting point of a 1:2 dioxane-iodine monochloride complex formed in the vapor phase.

Only one iodine pentafluoride complex is reported in the literature and that is a 1:1 complex with dioxane (51).

Skelly and Popov (41) determined the electrical conductance of some polyhalogen complexes in acetonitrile. The polyhalogen complexes such as $(CH_3)_4NIBr_2$ and $(CH_3)_4NIBrCl$ behaved as strong electrolytes.

The electric moments of the hydrogen halides measured in several solvents show that they form complexes with dioxane (65). Spectrophotometric studies (4) show that iodine, iodine monochloride and bromine interact to some extent with trifluoroacetic acid.

In the last several years, a considerable amount of work has been done on molecular complexes formed by metal halides with organic oxygen and nitrogen compounds. Curran and Wenzke (10, 11) reported electric moments of the mercuric halides in dioxane; however, they were probably actually measuring the moment of a mercuric halide-dioxane complex. In determining the solubility of aluminum bromide in pyridine from -10° to 70° C., Müller, et al. (34) found that several compounds were formed. I. A. Sheka, et al. (53-57) and H. Ulich, et al. (62, 63) have measured dipole moments of various metal halide complexes in benzene solution. These are tabulated in Table 2.

The aluminum halide complexes containing two moles of dioxane ($AlX_3.2C_4H_8O_2$) appear to dissociate in solution to give the monodioxane complex since the dipole moments for both complexes are identical.

It has been observed that the dipyridine complex of mercuric iodide (70) dissociates in benzene solution, probably into pyridine and a monopyridine complex. The monopyridine complex has been isolated and the heat of formation of mercuric halide and cupric halide complexes with pyridine have been measured (24) as listed in Table 3.

TABLE 2

ELECTRIC MOMENTS OF SOME METAL HALIDE COMPLEXES

Complex	μ D.	Complex	μ D.
$AlBr_3.2C_4H_8O_2$	5.23	$AlCl_3.C_6H_5NH_2$	6.86
$AlBr_3.C_4H_8O_2$	5.23	$AlCl_3.C_6H_5NO_2$	9.05
$Al_2Br_6.C_4H_8O_2$	4.62	$AlCl_3.C_6H_5COCl$	8.92
$AlCl_3.C_4H_8O_2$	5.19	$AlCl_3.(C_6H_5)_2CO$	8.72
$AlCl_3.2C_4H_8O_2$	5.19	$TlCl_3.2C_4H_8O_2$	3.66
$AlBr_3.Ph_2CO$	8.41	$TlCl_3.3C_5H_5N$	4.07
$AlBr_3.o\text{-}C_7H_7NO_2$	9.30	$TlCl_3.2C_9H_7N$	5.68
$AlBr_3.p\text{-}C_7H_7NO_2$	9.76	$BCl_3.(C_2H_5)_2O$	5.98
$AlBr_3$.Anisole	6.58	$BCl_3.CH_3CN$	7.65
$AlBr_3.o\text{-}ClC_6H_4NO_2$	9.56	$BCl_3.C_2H_5CN$	7.75
$AlBr_3.Ph_2NH$	6.68	$BeCl_2.2(C_2H_5)_2O$	6,84
$AlBr_3.Ph_2O$	6.56	$BeBr_2.2(C_2H_5)_2O$	7.57
$AlBr_3.H_2S$	5.14	$InBr_3.(C_2H_5)_2O$	5.04
$AlBr_3.(C_2H_5)_2O$	6.43	$TiCl_4.C_3H_7CN$	6.05
$AlBr_3.C_6H_5NO_2$	9.13	$TiCl_4.C_6H_5CN$	6.16
$AlCl_3.o\text{-}ClC_6H_4NO_2$	9.48	$SnCl_4.C_6H_5CN$	6.55
$AlCl_3.p\text{-}ClC_6H_4NO_2$	7.79	$SnCl_4.(C_2H_5)_2O$	3.60
$AlCl_3$.Anisole	6.54	$SnCl_4.2(CH_3)_2CO$	7.70
$AlCl_3o\text{-}C_7H_7NO_2$	8.92	$SnCl_4.2CH_3COC_6H_5$	8.70
$AlCl_3.p\text{-}C_7H_7NO_2$	9.68	$SnCl_4.2C_6H_5CHO$	7.50
$AlCl_3.(C_2H_5)_2O$	6.54		

TABLE 3

HEATS OF FORMATION OF CUPRIC AND MERCURIC HALIDE COMPLEXES WITH PYRIDINE

Complex	- Δ H kcal./mole
$CuCl_2$.2Pyridine	28.15
$CuBr_2$.2Pyridine	24.89
$CuBr_2$.6Pyridine	45.20
$HgCl_2$.Pyridine	11.14
$HgCl_2$.2Pyridine	17.22
$HgBr_2$.Pyridine	9.19
$HgBr_2$.2Pyridine	15.45
HgI_2.2Pyridine	15.22

The dioxane complexes of sodium, lithium and potassium iodides have been isolated (46). The alkali chlorides and bromides do not form complexes. The dioxane complexes of divalent metal halides have been studied by several investigators (47, 68, 69). Magnesium bromide forms stable 1:2 complexes with acetone, ethyl acetate and propanal (33), and with acetonitrile a 1:1 complex is formed. Magnesium bromide does not form stable complexes with fluorinated esters, aldehydes and nitriles. Complexes of the tin tetrahalides have also been prepared (45).

THEORY

Dipole Moment Measurement

Electric dipole moments are very useful in determining the structures of organic and inorganic compounds. The general theory of dipole moments and the derivation of equations pertaining to the theory are adequately described in the literature (3, 31, 58) so only a very brief outline will be presented here.

When two atoms of differing electronegativities are joined together by a chemical bond, the more electronegative atom will accumulate a negative charge and the remaining atom will be more positive in character. This separation of charge by some distance constitutes an electric dipole. The dipole moment is the product of the electrical charge and the distance of separation. This electric moment (μ) is a vector quantity since it possesses both magnitude and direction. Thus in a molecule composed of several atoms and having several individual bond moments, the total dipole moment is the vector sum of all the bond moments. The electronic charge is 4.8×10^{-10} e.s.u., so that if a positive and negative electronic charge are separated by 1 Å, which is a distance of the order of a bond length, a moment of 4.8×10^{-18} e.s.u. is created. This is generally reported as 4.8 Debye units.

The usual methods of obtaining the dipole moment of a substance depend upon measurement of the dielectric constant.

In an electric field, the electrons and nuclei are displaced from their mean positions so that both polar and non-polar molecules will become polarized. This polarization corresponds to individual moments m_E and m_A induced by displacement of the electrons and nuclei by the electric field F. If an electric field of unit strength induces the moments M_E and M_A in a non-polar molecule, then in a field of strength F, the average moment over all molecules is:

$$\bar{m} = (M_E + M_A)F \qquad (1)$$

This is often referred to as "induced" or "distortion" polarization.

If the molecules have a permanent dipole moment, rather than being nonpolar, they will tend to orient themselves to oppose the field. This alignment is disturbed by thermal agitation of the molecules. The resulting average orientation will be at some point between the original position of the dipole and the perfectly aligned position. The result is that a slight excess of dipoles will be in opposition to the field at any particular time and this corresponds to a further moment, the "orientation" polarization $\bar{m}_o$. This orientation polarization was first evaluated by Debye (13), with the aid of certain approximations. He found

$$\bar{m}_o = \frac{\mu^2 F}{3kT} \qquad (2)$$

where k is the Boltzmann constant and T is the absolute temperature. The total moment ($\bar{m}_t$) is then:

$$\bar{m}_t = \left(M_E + M_A + \frac{\mu^2}{3kT} \right) F \qquad (3)$$

To evaluate μ from experimental data, $\bar{m}_t/F$ must be replaced by another expression containing known or measurable quantities. This can be done by using the expression developed by O. F. Mosotti (1850) and R. Clausius (1879). Their equation was obtained by a consideration of the definition of the dielectric constant and the force acting upon a polar molecule at the center of a spherical cavity in a dielectric which has been placed in an electric field. They derived the relationship:

$$\frac{\bar{m}_t}{F} = \frac{M}{Nd} \cdot \frac{3}{4\pi} \cdot \frac{\varepsilon - 1}{\varepsilon + 2} \qquad (4)$$

where ε is the dielectric constant, M is the molecular weight, d is the density and N is Avagodro's number. Combining Equations 3 and 4 gives:

$$P_t = \frac{\varepsilon - 1}{\varepsilon + 1} \cdot \frac{M}{d} = \frac{4\pi N}{3} \left(M_E + M_A + \frac{\mu^2}{3kT} \right) \qquad (5)$$

as the complete expression for the total molecular polarization (P_t). The total polarization is equal to the sum of the electronic, atomic and orientation polarizations:

$$P_t = P_E + P_A + P_o \, . \qquad (6)$$

It should be noted that from assumptions made in its derivation Equation 5 is valid only for gases at pressures where the molecules exert no mutual influence on each other. With certain modifications, as will be shown later, it can be applied to dilute solutions of substances in non-polar solvents.

In order to make use of Equations 5 and 6 in the calculation of dipole moments, P_A and P_E must be evaluated or eliminated. If an alternating field is used in measuring the dielectric constant then, as the frequency is increased, a point is reached where the orientation polarization starts to decrease due to the fact that the inertia of the molecules prevents them from following the reversals of the field. Thus, as the frequency increases, the orientation polarization is completely eliminated and at still higher frequencies, the atomic polarization will likewise disappear for the same reason. At frequencies of the order of the wavelength of light only the electronic polarization (P_E) remains. Using Maxwell's relationship that for measurements carried out at the same frequency, $\mathcal{E} = n^2$, and measuring the refractive index at long wavelengths, the total polarization can be rewritten as:

$$P_t = MR = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d} \tag{7}$$

which is identical to the molar refraction (MR) as defined by the Lorenz-Lorentz formula. For a given substance this quantity is essentially constant and independent of temperature. Therefore by determination of the dielectric constant and density of a pure substance, $P_o + P_E + P_A$ can be found. From the molar refraction it is possible to estimate the electronic polarization and so obtain the orientation polarization by difference if P_A is known. Although MR should be determined at infinite wavelength it is customary to measure refractive indices at the wavelength of the sodium D line and use MR_D in place of MR_∞. The sum of the atomic and electronic polarizations ($P_A + P_E$) is often taken to be equal to MR_D. Some error is introduced by including P_A in this expression but P_A is usually small and can therefore be disregarded, or P_A may be estimated as about 10% of P_E.

Since the orientation polarization term is $\frac{4\pi N\mu^2}{9kT}$, we see that

$$P_T - MR_D = \frac{4\pi N\mu^2}{9kT} \tag{8}$$

or solving for μ and substituting the constants π, N and k

$$\mu = 0.0128\sqrt{(P_T - MR_D)T.} \tag{9}$$

The preceding equation applies to gases or vapors. With some modifications of the Clausius-Mosotti relation, the equation can be applied to dilute solutions of polar solutes in nonpolar solvents. Assuming that $P_{12} = P_1f_1 + P_2f_2$, the molar polarization of the solute can be expressed as:

$$P_2 = \frac{P_{12} - P_1}{f_2} - P_1 \tag{10}$$

where P_{12}, the molar polarization for the solution is:

$$P_{12} = \frac{\varepsilon_{12} - 1}{\varepsilon_{12} + 2} \cdot \frac{M_2f_2 + M_1f_1}{d_{12}} \tag{11}$$

where the subscripts 1, 2, and 12 refer to solvent, solute and solution, respectively, and f is mole fraction. By measuring a series of solutions containing low concentrations of solute, the corresponding P_2 values are obtained. These are then plotted graphically versus f_2 and the best straight line through the points extrapolated to zero concentration to give the true polarization (P_2^o) of the solute in the absence of solvent effects. This value of P_2^o is combined with the molar refraction (P_2^o - MR_D) and used in Equation 9 to compute the dipole moment.

An error is introduced in the dipole moments measured by this method, due to assumptions in the derivation of the equations. This error is assumed usually to have a maximum value of a few tenths of a Debye unit (66). The solvent effect, which is the difference between dipole moments measured in the gas phase and in dilute solutions of nonpolar solvents, is usually not greater than 0.2 D. (60).

The dipole moments in this work were calculated according to the method suggested originally by Hedestand (23) and modified by Halverstadt and Kumler (17). These workers have shown that both dielectric constant (ε_{12}) and density or specific volume ($1/d_{12} = V_{12}$) are usually linear functions of the mole fraction of solute for dilute solutions.

The relationship of the dielectric constant and density to mole fraction is then:

$$\varepsilon_{12} = \varepsilon_1(1 + \alpha f_2) \qquad (12)$$

$$d_{12} = d_1(1 + \beta f_2) \qquad (13)$$

where α and β are the slopes of the respective plots of dielectric constant and density versus mole fraction of solute f_2; also $\mathcal{E}_1$ and d_1 are the corresponding intercepts at infinite dilution.

The substitution of Equation 11 into Equation 10 results in the following expression:

$$P_2 = \frac{\mathcal{E}_{12} - 1}{\mathcal{E}_{12} + 1} \cdot \frac{M_2}{d_{12}} + \frac{f_1 M_1}{f_2}\left(\frac{\mathcal{E}_{12} - 1}{\mathcal{E}_{12} + 2} \cdot \frac{1}{d_{12}} - \frac{\mathcal{E}_1 - 1}{\mathcal{E}_1 + 2} \cdot \frac{1}{d_1}\right) \quad (14)$$

Substitution of Equations 12 and 13 into Equation 14, expansion of the resulting expression and simplification, gives the following equation:

$$P_2 = \frac{\mathcal{E}_{12} - 1}{\mathcal{E}_{12} + 2} \cdot \frac{M_2}{d_{12}} + \frac{f_1 M_1}{d_{12}}\left(\frac{3\alpha\mathcal{E}_1 - \beta\,(\mathcal{E}_1 - 1)[\mathcal{E}_1(1 + \alpha f_2) + 2]}{(\mathcal{E}_1 + 2)(\mathcal{E}_1(1 + \alpha f_2) + 2)}\right) \quad (15)$$

Now in the limit as $f_2 \longrightarrow 0$, $P_2 = P_2^{\infty}$, $d_{12} = d_1$ and $f_1 = 1$. Equation 15 then becomes:

$$P_2^{\infty} = \frac{3\alpha\mathcal{E}_1 M_1}{d_1(\mathcal{E}_1 + 2)^2} + \frac{M_2 - \beta M_1}{d_1} \cdot \frac{\mathcal{E}_1 - 1}{\mathcal{E}_1 + 2} \quad (16)$$

In this work, β' was calculated from plots of specific volume versus mole fraction and in this case $\beta' = \frac{-\beta}{d_1}$ and $\alpha' = \alpha\mathcal{E}_1$, so that Equation 16 simplifies to:

$$P_o^{\infty} = \frac{3\alpha' M_1 V_1}{(\mathcal{E}_1 + 2)^2} + (M_2 V_1 + \beta' M_1) \cdot \frac{\mathcal{E}_1 - 1}{\mathcal{E}_1 + 2} \quad (17)$$

This equation was used in all the calculations reported here. The values of $\mathcal{E}_1$ and V_1 used in the calculations were the accepted values for the pure solvent and not the extrapolated values of the ε_{12} versus f_2, and V_{12} versus f_2, plots. The extrapolated values of ε_1 and V_1, in most cases, agreed fairly well with the accepted values for pure solvent.

The additivity of bond refractions was assumed in the calculations of molar refractions (MR_D) and values of bond refractions reported by Vogel (64) were used.

To determine the dielectric constants of the solutions, it was necessary to calculate a cell constant for the experimental cell. This was done by measuring the capacitance of the cell at the desired temperature, filled first with dry air and then pure solvent. The cell constant (k) was calculated from the following equation:

$$k = \frac{C_{air} - C_s}{\varepsilon_1 - 1} \qquad (18)$$

where the values for ε_1, the dielectric constant of the solvent at 25° C., were as follows: benzene, 2.2725; dioxane, 2.2080; and carbon tetrachloride 2.2280. The dielectric constant of benzene at other temperatures was given (31) by the expression:

$$\varepsilon_t = \varepsilon_{25} + (\delta\varepsilon/\delta t)(t - 25) \qquad (19)$$

where $\delta\varepsilon/\delta t = -0.0019$. The dielectric constant of each solution was calculated from the following equation using the cell constant along with the capacitance readings for the cell filled with air and then filled with a solution of a concentration ($C_{soln.}$).

$$\varepsilon_{12} = \frac{(C_{air} - C_{soln.})}{k} + 1 \qquad (20)$$

The density of each solution was determined at the same temperature as the dielectric constant. The slopes α' and β' were determined from the data by the method of least squares and used in Equation 17 to determine the molar polarization. The dipole moment (μ) was calculated from Equation 9.

Cryoscopy

The depression of the freezing point of the solvent by solute in ideal solutions is a colligative property which is dependent on the concentration of the solute in solution and not on the nature of the solute. The slight pressure dependence of freezing point is usually disregarded since most measurements are made at atmospheric pressure which varies only slightly.

The depression of the freezing point ΔT_f is related to the mole fraction f_2 of the solute (if pure solvent separates as solid phase) by the equation:

$$\Delta T_f = \frac{RT_o^2 f_2}{L_f} \qquad (21)$$

where R is the gas constant, T_o is the freezing point of the pure solvent, and L_f is the molar heat of fusion of the solvent. This equation is useful in dilute solution where f_2 is small and it can be shown that:

$$\Delta T_f = K_f m \qquad (22)$$

where m is the molal concentration of the solute and K_f the molal freezing point depression constant and is defined by the equation:

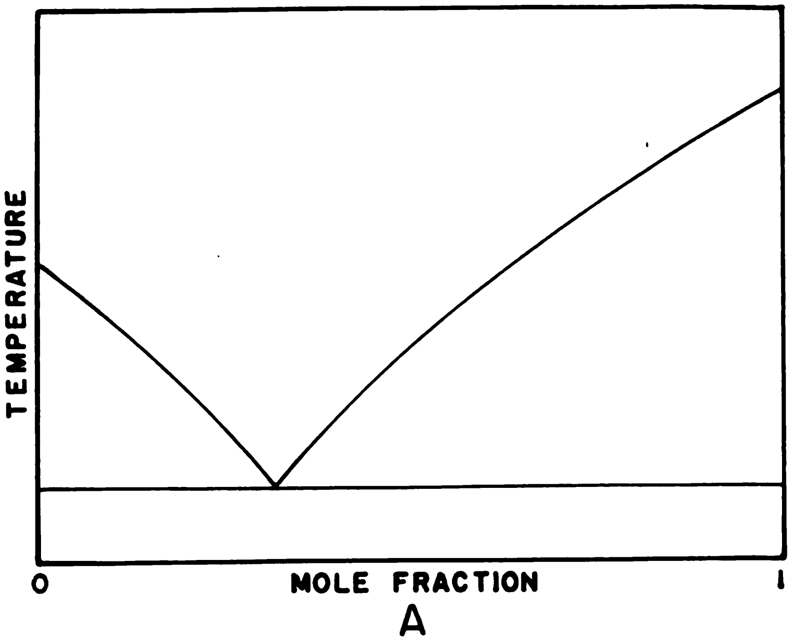
$$K_f = \frac{RT_o^2}{1000\ L_f/M_1} \qquad (23)$$

where M_1 is the molecular weight of the solvent.

For a condensed system of solid and liquid phases in equilibrium, the relationships can be expressed by a temperature-composition diagram. The curve of a temperature-composition diagram can be called either a "freezing-point depression curve" or a "solubility curve" since it illustrates both phenomena. The curve can be considered to represent the depression of the freezing point of the first substance by the second substance or the solubility curve of the second solid with the first as solute. The term "solubility" is used when the solid phase that separates is the solute, and "freezing point" when the solid is the solvent.

A general discussion of the many different kinds of phase diagrams of condensed systems can be found in the literature (15, 16, 43). A system of two components can show a number of different types of composition-temperature diagrams. Diagram A of Figure 1 is a simple system showing a single eutectic point and two freezing-point curves. Diagram B of Figure 1 represents a more complicated system in which the two components form a compound in a 1:1 ratio. This diagram also shows solid solution of the 1:1 compound in the one component.

Since the variables of a condensed system are composition and temperature, the methods for determination of phase diagrams can be classified as either isothermal or isoplethal.



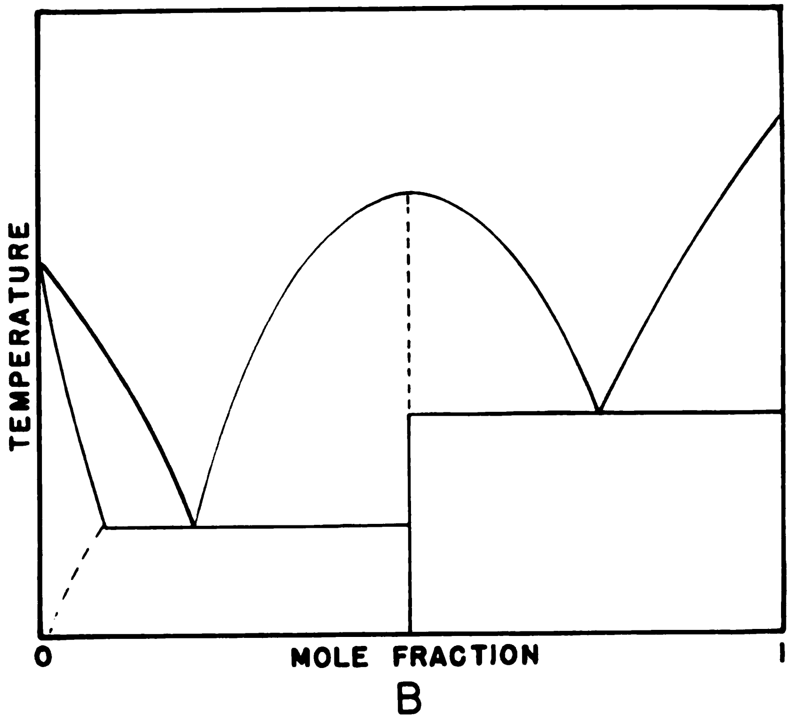


Figure 1. Some phase diagrams of two component systems.

Isothermal methods involve the determination of the solubilities at known temperatures. For solid-liquid solubility curves this may be accomplished by the separation of the phases at equilibrium followed by analysis of the phases. The isolation of the liquid from the solid is often difficult, especially if one component is volatile or if the solid is very finely divided, mechanically retaining the liquid.

The composition of the saturated solution may be determined without separation from the solid by plotting isothermally some property of the liquid as a function of composition. Starting with an unsaturated solution the property will vary smoothly with composition until the solution is saturated at which point a break will occur. If this is performed at enough temperatures the plot of composition versus temperature can be worked out.

Isoplethal methods involve the measurement of the temperature of phase transition. One of the simplest of the isoplethal methods is the visual method in which the temperature of appearance or disappearance of a particular phase is observed. This has an advantage in that it can be repeated on the same sample for checking results. For solid-liquid systems this is very readily applied to the first appearance of crystals from solution.

The method of thermal analysis is applicable in those cases in which a sample is heated above the phase transition point, allowed to cool under controlled conditions, and a plot made of temperature versus time. The break in the temperature-time curve corresponds to the phase transition and is due to the evolution of the heat of transition of the material.

The method of dilatometry is similar to that of thermal analysis. The volume of the sample of known composition is plotted versus temperature at constant pressure. Since time is not a variable in this method, the sample may be held at a constant temperature to insure equilibrium in the sample. This method overcomes the question of internal equilibrium in the thermal method.

EXPREIMENTAL

Dielectric Constants

The dielectric constants were measured by use of an apparatus employing the heterodyne beat method, in which the frequencies of two oscillating circuits are matched. One of these circuits contains a two hundred kilocycle quartz crystal which serves as the control element in the fixed frequency circuit. The other circuit contains the experimental cell, a variable precision condenser (General Radio, Type 722D), and an inductance which are connected in parallel in one of the tuned circuits of the variable frequency oscillator. The frequency ν of this second circuit is given approximately by:

$$\nu = \tfrac{1}{2}\pi\sqrt{LC} \qquad (24)$$

where L is the inductance and C the capacitance. Changes in the cell capacitance must be matched by a compensating change in the precision condenser.

The oscillations from the two circuits are fed into a mixer tube (6SA7) where the emerging frequency is the difference of the two. This is detected by a speaker, the pitch decreasing as the frequencies are matched. For more sensitive detection of the null point a "Magic Eye" indicator tube (6E5) was used. This apparatus is very similar to that described by Chien (8).

When measuring the dielectric constant, the frequencies of the two circuits are matched with air in the cell and then a solution is placed in the cell. The change in capacitance of the cell on introducing the sample must be matched by a change in the capacitance of the precision condenser to bring the frequency back to the null condition again. From the readings of the precision condenser with air and with solution in the cell the dielectric constant of the solution may be computed with the aid of Equation 20.

The experimental cell (Figure 2) consisted of three concentric nickel cylinders with the middle cylinder at high potential and shorter than the two grounded cylinders. The cylinders are separated by small Teflon spacers and the outer cylinder serves as the wall of the cell. The cell is filled with about ten milliliters of the solution to be measured and allowed to come to temperature equilibrium with the bath in which the cell is immersed. The temperature in the bath was maintained 25.00 ± 0.02° C. by use of a "Fisher Electronic" relay in conjunction with a knife heater. A motor driven stirrer was used to minimize temperature gradients in the bath.

In general five or six solutions of a particular solute at concentrations varying from 0.0005 to 0.02 mole fraction were prepared and measured the same day. In some cases (fluoride complexes) preparation and measurement were completed in a few hours to minimize any reaction. After the capacitance change of a solution had been measured, the solution was transferred

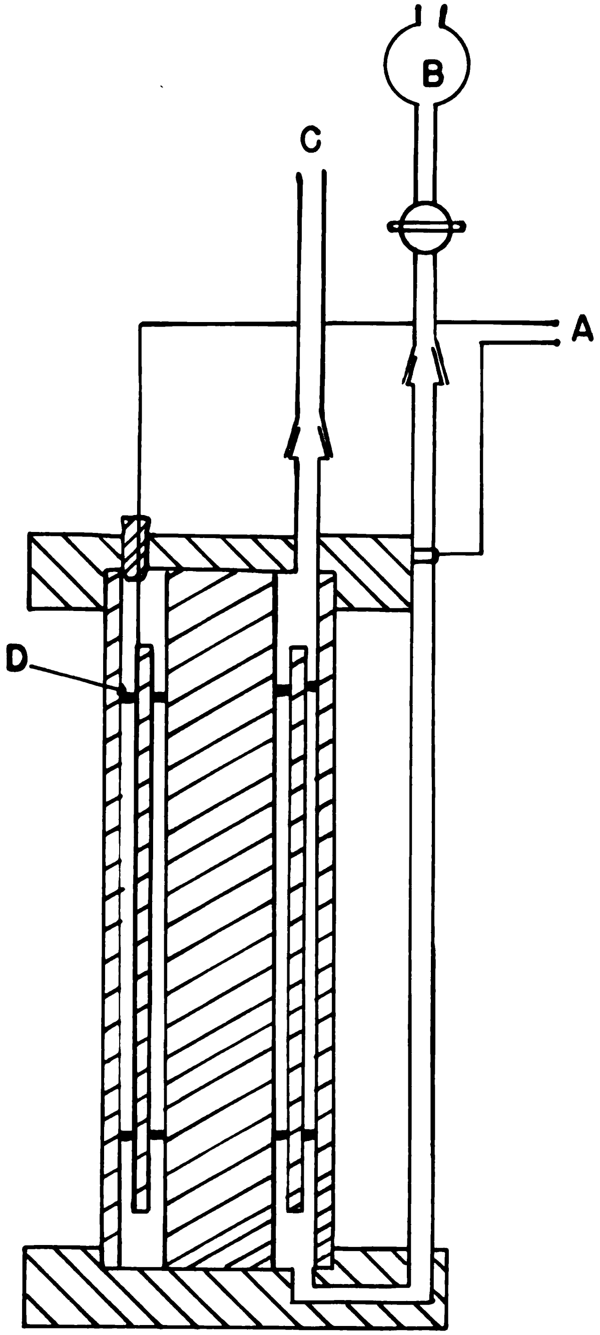


Figure 2. The experimental cell used for dielectric constant measurements: A, to circuit; B, solution flask; C, to dry air and air outlet; D, Teflon spacers.

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directly from the cell into a modified Ostwald-type pycnometer (48) for density determination. All weights were corrected for the buoyant effect occuring when weighing materials in air with brass weights.

The compounds, complexes and nonpolar solvents used were prepared and purified as described in a later section.

Dissociation Constants

The dissociation constants were determined by a spectrophotometric method. A Beckman DK-2 spectrophotometer was used with capped quartz cells for the measurements. The measurements were made at room temperature (about 25° C.). A weighed quantity of a standard solution of halogen in carbon tetrachloride was placed in the sample cell. The spectrum was determined using carbon tetrachloride in the reference cell. Then a known quantity of amine was added to the sample cell and the spectrum redetermined. This procedure was continued until there was very little or no change in the spectrum on further addition of amine.

The extinction coefficient (a_c) of the complex was then calculated from the final spectrum using the equation:

$$A = a_c \cdot b \cdot c \qquad (25)$$

where A was the total absorbance, b the path length in centimeters through the cell and c the concentration in moles/liter. The concentration of the complex was assumed to be the same as the original concentration of halogen.

From the spectra of the 1:1 complex at various concentrations in carbon tetrachloride solution, the degree of dissociation (x) was calculated from the equation:

$$A = a_x \cdot b \cdot xc + a_c \cdot b \cdot c(1 - x) \qquad (26)$$

where a_x was the extinction coefficient of the halogen at the wave length of the complex absorption peak.

The dissociation constant (k'_c) was calculated from Ostwald's dilution law[1].

$$k'_c = \frac{x^2c}{1 - x} \qquad (27)$$

It should be noted that k'_c might not be a constant because of the neglect of activity coefficients.

Iodometric Equivalent

The amount of elemental halogen in the molecular complexes was determined experimentally in the manner described below. The calculated value was found by dividing the molecular weight of the complex by the number of elemental halogen atoms considered to be present in the complex.

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[1] S. Glasstone, Textbook of Physical Chemistry, D. Van Nostrand Co. Inc., 1946, p. 955.

Samples of the complex weighing between two and three milliequivalents were dissolved in 10 ml. of pyridine. Six grams of C. P. potassium iodide were added and the mixture cooled in an ice bath. To the cold mixture 12 ml. of 12 N. hydrochloric acid were slowly added. Heat is evolved and pyridine-hydrochloride generally percipitates and carries with it a quantity of iodine. The mixture was titrated with 0.1 N. sodium thiosulfate.

After the titration had started 10 ml. of acetone were added. The acetone would dissolve the pyridine-hydrochloride and liberate the iodine. The solution was deep red at this point and usually contained some undissolved potassium iodide. The titration was continued until a yellow color was reached, then about 20 ml. of water added. Any remaining potassium iodide would dissolve and the solution would be a clear yellow color. Two ml. of starch solution were added and the titration continued to the starch endpoint. A blank was determined on the indicator and components.

Freezing Point Measurements

The measurement of the freezing points of pure liquids and solutions, for determining points on a solid-liquid phase diagram, were carried out using the following apparatus.

The experimental cell (Figure 3) was constructed of "Pyrex" glass having an air space between the inner and outer wall of the cell which could be evacuated to control the rate of cooling of the sample. The cell was fitted with a

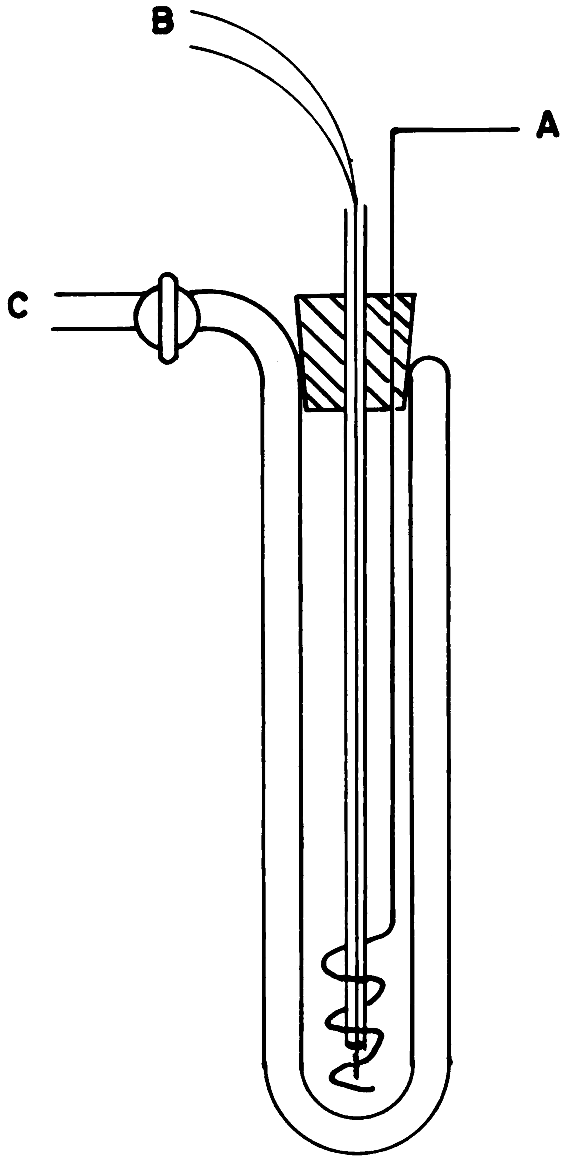

Figure 3. Freezing point cell: A, stirrer; B, thermocouple leads; C, to vacuum pump.

fluorothene[1] plug with openings for the stirrer and the thermocouple leads. The thermocouple was constructed of Leeds and Northrup 24 gauge copper wire and constantan wire. The junction on the thermocouples were silver-soldered. The thermocouple junction in the cell was sealed through a glass tube and the emerging tip was immersed directly in the solution. By this means the chance of temperature differential existing between the sample and the measuring device was greatly reduced. The reference junction was immersed in a Dewar flask filled with crushed ice and purified water.[2]

The ice employed was frozen from purified water in a closed polyethylene container. The temperature of this cold junction was assumed to be 0.00° C. The thermocouple was calibrated at the following check points: melting point of carbon tetrachloride, -22.90° C.; transition point of sodium sulfate heptahydrate to sodium sulfate decahydrate, 32.38° C.; and transition point of anhydrous sodium bromide to sodium bromide dihydrate, 50.67° C. These check points not only serve to calibrate the thermocouple, but the entire measuring circuit, since the same standard cell, galvanometer and precision potentiometer were employed throughout all the calibration and experimental

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[1] Teflon as used throughout this thesis is the registered trade name of the E. I. DuPont de Nemours & Co. for the tetrafluoroethylene polymer. Fluorothene is a trifluorochloroethylene polymer.

[2] Distilled water was run through a mixed-bed ion-exchange column. A metering device on the column indicated less than one part per million of sodium chloride.

work. Since the measured potentials at the check points agreed to within 1 x 10^{-6} volt with the standard potentials for a copper-constantan thermocouple (25) no correction was applied to the measured potentials.

The stirrer was constructed of nickel wire and activated by a windshield wiper motor.

The cell was immersed in an unsilvered Dewar flask which contained methanol (Figure 4). The bath was cooled by circulating the methanol with a centrifugal pump through a copper tube and a reservoir contained in a second Dewar flask which was cooled with Dry Ice and acetone. A stopcock in the line controlled the flow of the cold methanol from the reservoir and therefore the temperature in the unsilvered Dewar flask. By a combination of flow rate and pressure in the jacket of the cell, any desired cooling rate of the sample could be attained. The cooling rate of the sample was generally about one degree per minute.

For handling and measuring the iodine pentafluoride with a minimum of exposure to moisture, a special burette was constructed (Figure 5). A two milliliter Pyrex pipette tube was scribed at 0.1 inch intervals along its entire length with a diamond point. A Teflon stopcock (Lab Crest) was sealed on the bottom of the tube. The top of the tube was fitted with a fluorothene adapter that connected the burette to a drying tube. This tube could be replaced by an aspirator bulb for filling the burette. The calibration data of the burette with mercury

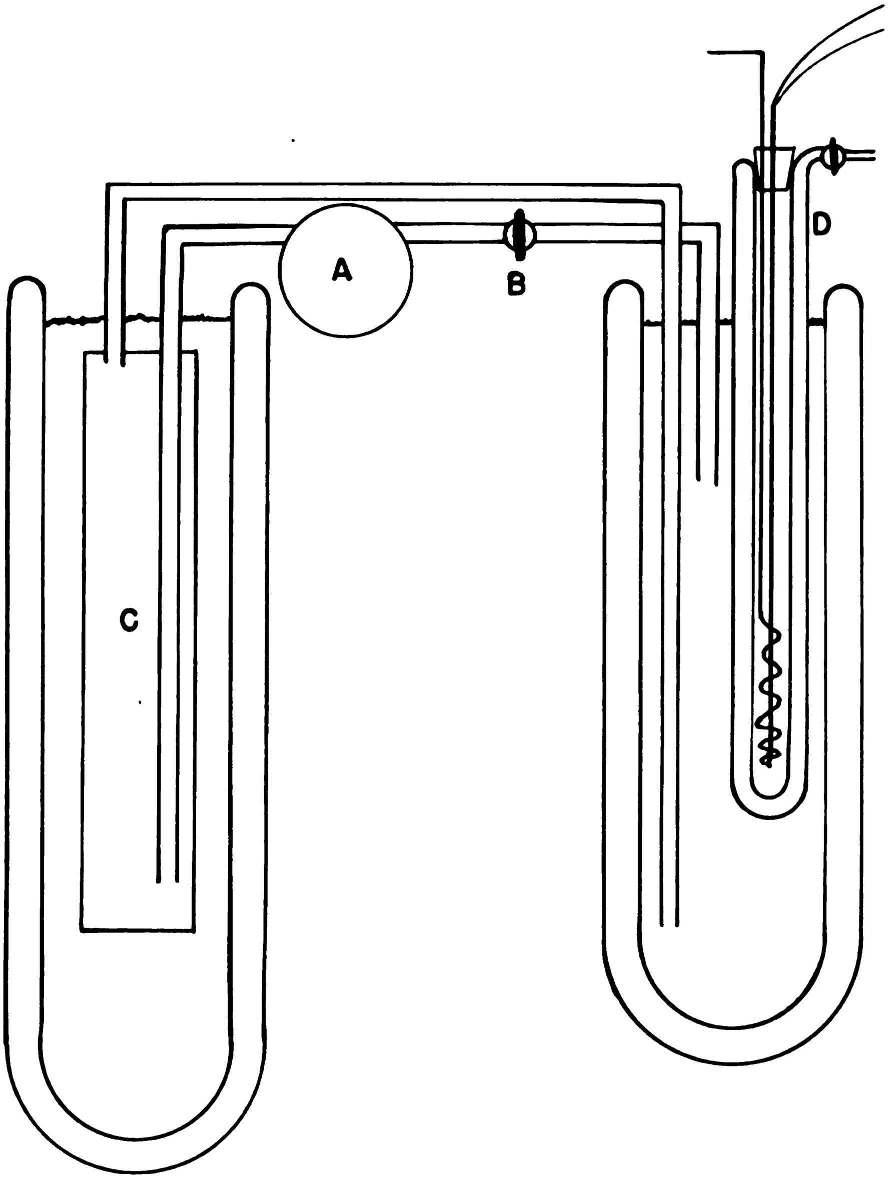

Figure 4. Freezing point cell and cooling bath arrangement: A, circulating pump; B, valve; C, reservoir; D, freezing point cell.

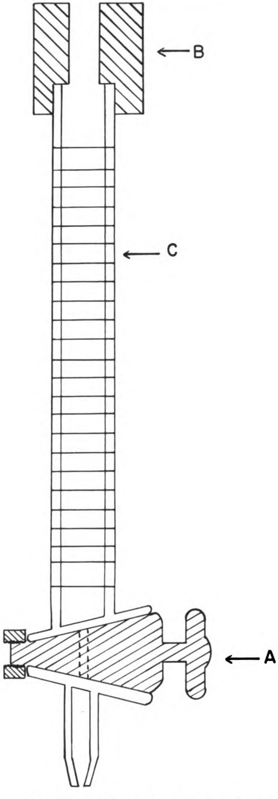

Figure 5. Iodine pentafluoride measuring burette: A, Teflon stopcock; B, fluorothene adapter; C, calibrated tube.

is given in Table 4. A special tube was constructed of fluorothene to fit over the tip of the burette and lead into a container of iodine pentafluoride. When suction was applied at the top of the tube, iodine pentafluoride would be drawn into the burette. During this filling operation, the container of iodine pentafluoride and the bottom half of the burette were encased in a polyethylene bag. The atmosphere in the bag was flushed out with dry nitrogen to remove the water vapor in the atmosphere before the filling operation commenced. When the burette was filled, a fluorothene cap was placed over the tip and the drying tube connected on the top of the burette. Knowing the density of iodine pentafluoride at a given temperature and the volume added to the solvent, the weight of the solute can be determined.

The temperature measuring circuit (Figure 6) contained both a precision potentiometer[1] and an electronic recording potentiometer with a direct-current amplifier[2]. The circuit was so arranged that the thermocouple output could be measured with the precision potentiometer or the path of the cooling curve could be followed on the recorder. The potentiometer in the recorder circuit was necessary in order to supply a bucking

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[1] A type K-2 potentiometer made by the Leeds and Northrup Company of Philadelphia, Pennsylvania was used.

[2] A Leeds and Northrup type 9835B direct current amplifier was used in conjunction with a Brown electronic recorder made by the Minneapolis Honeywell Company, Minneapolis, Minnesota.

TABLE 4

CALIBRATION DATA FOR THE IODINE PENTAFLUORIDE BURETTE

Burette Reading	Wt. of Mercury	Average Weight per Division
0-5$^+$	2.0759	0.4151
5$^+$-10	2.0359	.4072
10-15	2.0929	.4186
15-20	2.0465	.4093
20$^-$-26	2.5185	.4197
26-30	1.6439	.4110
30-35	2.0717	.4143
35-40$^+$	2.1230	.4246
40-45	2.0685	.4137
45-50	2.0644	.4129
50-56	2.5065	.4177
56-60	1.7228	.4307
60-65	2.0396	.4079
65-70	2.1056	.4211
70-75	2.1155	.4231
75-80	2.0949	.4189
80-85	2.1075	.4215
85-90	2.1391	.4278

Average weight per division: 0.4174 grams

Average volume per division: 0.03083 milliliters

Total calibrated volume: 2.7752 milliliters

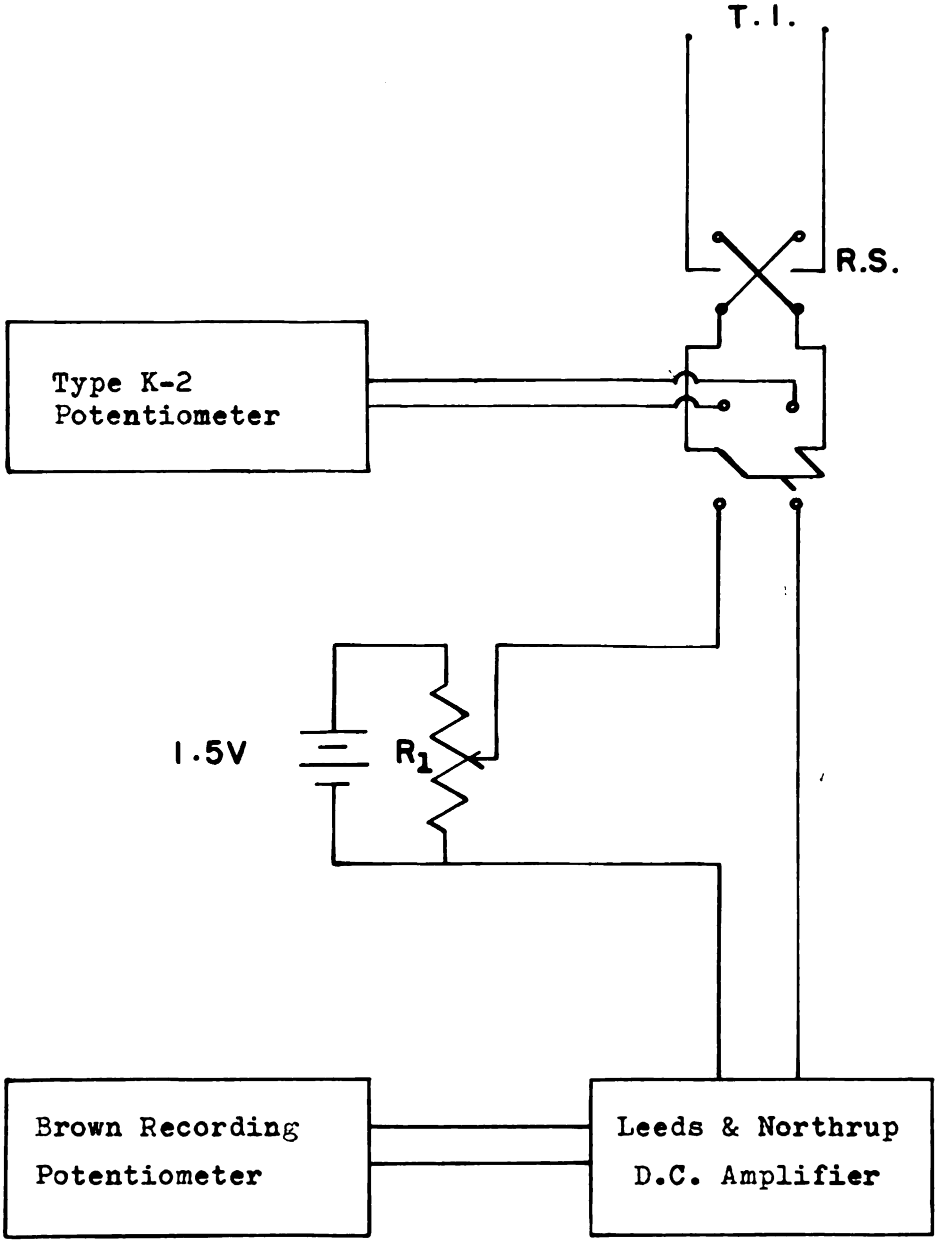

Figure 6. Temperature-measuring circuit: T.I., thermocouple input; R.S., switch for reversing the input to the recorder and potentiometer; R_1, student potentiometer used to obtain the bucking voltage.[1]

voltage to reduce the output of the output of the thermocouple. The output was reduced to such a magnitude that when amplified, the recorder had a sensitivity of 1.25 degrees per inch.

Preparation and Purification of Compounds

Benzene. This compound was purified by the following procedure. The major portion of a quantity of C. P. thiophene-free benzene was frozen and the liquor poured off. The residue was melted and the freezing operation repeated. The residue was then melted again, dried with calcium chloride, and distilled and stored over sodium. The density measured at 25° C. was 0.87336.

Quinoline. This compound was purified by drying Eastman White label material over anhydrous potassium carbonate, distilling and collecting the middle fraction.

Carbon Tetrachloride. This compound was purified by freezing a major portion of C. P. material, pouring off the liquor, melting the residue and then distilling this material from calcium hydride. The middle fraction, which distilled at 76.8° C., was collected. The density measured at 25° C. was 1.5844.

2,6-Dimethylpyridine. This compound was purified by refluxing "Eastman Yellow Label" 90% 2,6-dimethylpyridine with methyl benzene sulfonate for one hour. The mixture was cooled and the upper layer separated and distilled. The distillate was dried with calcium hydride and fractionally distilled. The middle fraction distilling at 142° C. at 737 mm. was used in this work.

2-Fluoropyridine. This compound was prepared by diazotization of 2-aminopyridine in 40% fluoroboric acid at a temperature below 5° C. After standing in ice for one hour, the solution was warmed to 40° C. to complete decomposition. The solution was neutralized with sodium carbonate after cooling to 5° C. The 2-fluoropyridine was extracted from the solution with ether. Fractional distillation of the ether layer gave a product distilling at 125° C. at 742 mm. (50). No evidence of decomposition was indicated after several weeks.

3-Fluoropyridine. This compound was prepared from 3-aminopyridine as described for 2-fluoropyridine. The product distilled at 106° C.

Trifluoroacetic Anhydride. This compound was prepared by refluxing trifluoroacetic acid over phosphorous pentoxide and distilling from fresh phosphorous pentoxide. The material distilled at 40° C.

Pyrazine. This compound was obtained from Wyandotte Chemicals Corporation, Wyandotte, Michigan, and was used without further purification.

2-Methylpyrazine. This compound was "Eastman White Label" and was used without further purification.

2-Bromopyridine. This compound was "Eastman White Label" and was used without further purification.

2-Chloropyridine. This compound was "Eastman White Label" and was used without further purification.

Dioxane. This compound was purified by freezing a major portion of C. P. dioxane, decanting off the liquor, melting the residue and repeating the freezing operation. The residue was then dried with anhydrous potassium carbonate and distilled. The middle fraction distilled at 101° C. and had a freezing point of 11.66° C. It was stored in a brown bottle over fresh sodium ribbon.

Iodine Bromide. This compound was prepared by addition of bromide to iodine and warming to complete solution. The iodine bromide crystallizes on cooling. The material was purified by fractional crystallization from the melt. The melting point of the final material was 41.5° C. compared to a value of 42° C. reported in the literature (9).

Iodine Trichloride. This compound was prepared by addition of iodine to condensed chlorine in a flask cooled by Dry Ice. The solid product was transferred for storage into a covered fluorothene beaker in a dry box (2).

Iodine Monochloride. This compound was prepared by adding an equivalent amount of iodine to a flask containing liquid chlorine cooled by dry ice. The compound was fractionally crystallized from the melt. It had a melting point of 27° C. (9).

Iodine Pentafluoride. This compound was obtained from a supply purified by H. Bradford Thompson (61).

Pyridine-Iodine Monochloride Complex. This complex was prepared by slow addition of a carbon tetrachloride solution of iodine monochloride to an equivalent amount of pyridine in carbon tetrachloride. The complex precipitated from solution and was filtered, washed with carbon tetrachloride and air dried. The complex was pale yellow in color and had a melting point of 129-131° C. compared to literature values of 132-134° C. (**14, 19, 40, 67**). Iodometric equivalent for the complex was 119.9 as compared to a calculated value of 120.7.

Pyridine-Iodine Bromide Complex. This complex was prepared in the same manner as the pyridine-iodine monochloride complex. The complex is bright yellow in color and after recrystallization from methyl alcohol had a melting point of 112-113° C. as compared to literature value of 113-117° C. (**14, 40, 67**). Iodometric equivalent for the complex was 143.1 as compared to a calculated value of 142.9.

Pyridine-Iodine Trichloride Complex. This complex was prepared by adding a solution of pyridine in carbon tetrachloride to the iodine trichloride solution. The complex was filtered and washed with carbon tetrachloride. The complex was bright yellow and evolved chlorine on heating. Some of the complex evidently converted to the monochloride complex on heating. It melted over a range of 142-146° C. and was evolving a gas on melting. Iodine equivalent was 77.4 compared to a calculated value of 78.1. The complex is fairly stable at room temperature.

Quinoline-Iodine Monochloride Complex. This complex was prepared in the same manner as the pyridine-iodine monochloride complex. It has a light cream color and has a melting point of

154-155° C. Iodometric equivalent was 145.4 as compared to a calculated value of 145.7.

Quinoline-Iodine Bromide Complex. This complex was prepared in the usual manner. The complex is yellow and has a melting point of 128-129° C. Iodometric equivalent was 168.6 as compared to a calculated value of 168.0.

Quinoline-Iodine Trichloride Complex. This complex was prepared in the same manner as the pyridine-iodine trichloride complex. It has a yellow color and a melting point of about 132° C. It evolves chlorine on heating. Iodometric equivalent was 94.1 as compared to a calculated value of 90.6.

2.6-Dimethylpyridine-Iodine Monochloride Complex. This complex was prepared in the usual manner. It has a yellow color and a melting point before and after recrystallization from methyl alcohol of 98-99° C. as compared to a literature value of 112-113° C. (40). Iodometric equivalent was 132.0 as compared to a calculated value of 134.7.

2,6-Dimethylpyridine-Iodine Bromide Complex. This complex was prepared in the usual manner. This complex was recrystallized from hot carbon tetrachloride and has an orange color. The melting point was 105-107° C. as compared to literature value of 106-108° C. (40). There appeared to be some decomposition at the melting point. The iodine equivalent was 156.7 as compared to a calculated value of 156.9.

2,6-Dimethylpyridine-Iodine Trichloride Complex. This complex was prepared in the same manner as the pyridine-iodine trichloride complex. It loses chlorine slowly at room temperature. It has a bright yellow color, evolves chlorine on heating and melts over the range of 90-95° C. Iodometric equivalent was 90.5 as compared to a calculated value of 85.1.

Pyrazine-Iodine Monochloride Complex. This complex was prepared in the usual manner. It has a dirty yellow color and sublimes on heating. It decomposes at 193° C. Iodine crystals appear on the sides of the container after several days indicating decomposition of the complex.

Pyrazine-Iodine Bromide Complex. This complex was prepared in the usual manner. It has an orange-brown color and sublimes on heating. It decomposes at 156° C.

2-Methylpyrazine-Iodine Monochloride Complex. This complex was prepared in the usual manner. It was yellow in color and decomposed to a black tar in a few days with the evolution of considerable gas.

2-Methylpyrazine-Iodine Bromide Complex. This complex was prepared in the usual manner. It has a yellow-orange color, sublimes upon heating and decomposes at 115° C.

2-Fluoropyridine-Iodine Monochloride Complex. This complex was prepared in the usual manner. Since the complex is quite soluble in carbon tetrachloride, it was necessary to concentrate the solution before the complex would crystallize in long yellow needles from the solution. It has a melting point of 56° C. Iodometric equivalent was 130.9 as compared to a calculated value of 129.7.

2-Fluoropyridine-Iodine Bromide Complex. This complex was prepared in the usual manner. It was necessary to concentrate and cool the carbon tetrachloride solution before the complex would crystallize in orange-brown needles. It has a melting point of 44-45° C.

2-Fluoropyridine-Iodine Trichloride Complex. This complex was prepared in the same manner as the pyridine-iodine trichloride complex. It precipitates readily from solution. It has a bright yellow color, evolves chlorine on heating and melts over the range of 56-65° C. Iodometric equivalent was 101.6 as compared to a calculated value of 82.5.

2-Chloropyridine-Iodine Monochloride Complex. This complex was prepared in the usual manner. This yellow complex was recrystallized from methanol and had a melting point of 80-82° C. Iodometric equivalent was 139.3 as compared to a calculated value of 138.0.

2-Chloropyridine-Iodine Bromide Complex. This complex was prepared in the usual manner. It crystallizes in orange-brown needles from methanol and has a melting point of 43-45° C. Iodometric equivalent was 163.2 as compared to a calculated value of 160.4.

3-Fluoropyridine-Iodine Monochloride Complex. This complex was prepared in the usual manner. The 3-fluoropyridine complexes are less soluble in carbon tetrachloride than the 2-fluoropyridine derivatives which makes their separation from solution easier. It crystallizes in yellow needles and has a melt

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melting point of 95-97° C. It tends to sublime upon heating. Iodometric equivalent was 129.7 as compared to a calculated value of 130.9.

3-Fluoropyridine-Iodine Bromide Complex. This complex was prepared in the usual manner. It crystallizes in yellow-tan needles and has a melting point of 70-72° C. Iodometric equivalent was 154.7 as compared to a calculated value of 152.0.

3-Bromopyridine-Iodine Monochloride Complex. This complex was prepared in the usual manner. It has a yellow color and a melting point of 90-92° C.

3-Bromopyridine-Iodine Bromide Complex. This complex was prepared in the usual manner. It has a yellow-orange color and a melting point of 77-78° C.

Dioxane-Iodine Monochloride Complex. This complex was prepared in the usual way. The crystals are red-yellow in color and have a melting point of 92-93° C. as compared to literature values of 56-58° C. (44). This complex is unstable and decomposes into dark colored material after several days.

3-Chloropyridine-Iodine Monochloride Complex. This complex was prepared in the usual manner. The lemon-yellow material was recrystallized from methanol and had a melting point of 56° C.

3-Chloropyridine-Iodine Bromide Complex. This complex was prepared in the usual manner. The yellow-orange complex was recrystallized from methanol and had a melting point of 47° C.

4-Chloropyridine-Iodine Monochloride Complex. This complex was prepared in the usual manner. The pale yellow complex was only moderately soluble in boiling methanol. It has a melting point of about 224-226° C. On heating the complex undergoes two changes: at about 100° C., it changes to an orange-brown colored solid and at about 205° C. it changes to a yellow colored solid. The limited solubility and high melting point indicate a certain amount of ionic character.

4-Chloropyridine-Iodine Bromide Complex. This complex was prepared in the usual manner. The complex was a yellow-brown color and was slightly soluble in methanol. It had a melting point of about 193-195° C.

Dioxane-Iodine Bromide Complex. This complex was prepared by slow addition of the halide to pure dioxane. It was filtered and washed with a small amount of carbon tetrachloride. The complex has a dark red-brown color and has a melting point of 64° C. compared to a literature value of 65° C. (44). It is unstable and decomposes into a dark red tar within a few days.

Dioxane-Iodine Pentafluoride. This complex was prepared in a dry box by slow addition of iodine pentafluoride to pure dioxane. The complex was then washed with carbon tetrachloride and dried on a suction filter. It is white and has a melting point of 112° C. when dropped on a hot stage. After melting it immediately decomposes giving a cloud of iodine vapor. The melting point compares with the value 112° C. reported by Scott and Bunnet (51). The complex can be recrystallized from hot benzene if great care is exercised to prevent water vapor from coming in contact with the solution. It can be stored without decomposition at -78° C.

Other Iodine Pentafluoride Complexes. The following complexes were prepared by mixing equivalent amounts of the indicated second component with iodine pentafluoride: 2-methylpyrazine-iodine pentafluoride, trifluoroacetic anhydride-iodine pentafluoride and pyridine-iodine pentafluoride. All these complexes are liquids at room temperature.

Table 5 summarizes the new molecular complexes that have been prepared and reported for the first time. Table 6 lists the carbon, hydrogen and nitrogen analyses for several of the molecular complexes as reported by the Spang Microanalytical Laboratory, Ann Arbor, Michigan.

1,2-Dichloroperfluorocyclopentane. An attempt was made to prepare 1,2-dichloroperfluorocyclopentane from 1,2-dichloroperfluorocyclopentene-1 (obtained from the Hooker Chemical Co.) by fluorination in the vapor phase with cobalt trifluoride. Three one-inch copper tubes were filled with cobalt trifluoride suspended on steel wool. These tubes connected in series were placed in tube furnaces, so that there was a temperature gradient between the inlet and outlet of the tube of about 150° C. The inlet temperature was about 100° C.

The material to be fluorinated was introduced through a dropping funnel into a heated flask where it vaporized and the vapor was subsequently carried by a stream of helium gas through

TABLE 5

SOME PROPERTIES OF NEW MOLECULAR COMPLEXES OBTAINED IN THIS INVESTIGATION

Complex	Color	M.p. °C.	Stability at room temp.
Pyridine.ICl_3	yellow	142.6	loses Cl_2
Quinoline.ICl_3	yellow	132	stable
2,6-Dimethylpy.ICl_3	yellow	90-95	loses Cl_2
2-Fluoropyridine.ICl_3	yellow	56-65	loses Cl_2
Quinoline.ICl	cream	154-5	stable
Pyrazine.ICl	yellow	dec. 193	unstable
2-Methylpyrazine.ICl	yellow	dec. 115	unstable
2-Fluoropyridine.ICl	yellow	56	stable
2-Chloropyridine.ICl	yellow	80-82	stable
3-Fluoropyridine.ICl	yellow	95-7	stable
3-Bromopyridine.ICl	orange	90-2	stable
3-Chloropyridine.ICl	yellow	56	stable
4-Chloropyridine.ICl	yellow	224-6	stable
Quinoline.IBr	yellow	128-9	stable
Pyrazine.IBr	orange	dec. 156	stable
2-Methylpyrazine.IBr	orange	dec. 115	stable
2-Fluoropyridine.IBr	orange	44-5	slow decomp.
2-Chloropyridine.IBr	orange	44-5	stable
3-Fluoropyridine.IBr	tan	70-2	stable
3-Bromopyridine.IBr	orange	77-8	stable
3-Chloropyridine.IBr	orange	47	stable
4-Chloropyridine.IBr	tan	193-5	slow decomp.

TABLE 6

ANALYSES OF MOLECULAR COMPLEXES

Complex	Calculated			Reported		
	%C	%H	%N	%C	%H	%N
Quinoline.IBr	32.16	2.09	4.16	32.13	2.06	4.23
Quinoline.ICl	37.07	2.42	4.30	36.65	2.40	4.92
2-Chloropyridine.ICl	21.76	1.46	5.07	21.54	1.47	5.33
2-Chloropyridine.IBr	18.74	1.25	4.37	18.65	1.13	4.36
Pyridine.IBr	20.99	1.76	4.89	21.23	1.84	5.05
2,6-Dimethylpy.IBr	26.77	2.88	4.46	26.64	2.87	4.44
3-Fluoropyridine.ICl	23.14	1.55	5.39	23.02	1.56	5.35
2-Fluoropyridine.ICl	23.14	1.55	5.39	23.18	1.55	4.90
3-Chloropyridine.ICl	21.76	1.46	5.07	21.94	1.44	5.06

the fluorination tube to a cold trap where the fluorinated material was condensed. This crude material was then fractionated to obtain the desired product. The major portion of the material distilled at 85° C. and solidified on cooling. The melting point was 30° C. The starting material has a boiling point of 89.5-91° C. and probably is very hard to separate from the product by fractional distillation. Cooling curves of the purest material obtained by fractional crystallization and sublimation still indicated that it was not a pure compound. This material had a melting point of 34° C. The solid material can be sublimed into white crystals that turn into an amorphous glass on standing.

RESULTS

The experimentally determined dielectric constants (ε_{12}) and specific volumes (V_{12}) of the solutions at the various temperatures are compiled in Tables 7 through 11. The graphical plots of dielectric constant versus mole fraction (f_2) are shown in Figures 7 through 19. The slopes α' and β' are listed in Table 12 along with the molar polarization of the solute at infinite dilution (P_2^{∞}) calculated using Equation 17. The molar refractions (MR_D) calculated from empirical constants (15), and the dipole moments (μ) obtained using Equation 9 are listed in Table 12 also.

The cryoscopic data for the pyridine-iodine pentafluoride system and the dioxane-iodine pentafluoride system are reported in Tables 13 and 14 respectively. The graphical plots of freezing point versus mole fraction of solute are shown in Figures 20 and 21.

The spectroscopic data for the halogen-amine systems investigated are reported in Tables 15 and 16. The spectra of these systems are shown in Figures 22 through 26.

TABLE 7

DIELECTRIC CONSTANTS AND SPECIFIC VOLUMES OF THE BENZENE SOLUTIONS AT 15° C.

f_2	ε_{12}	v_{12}
Dioxane-Iodine Pentafluoride Complex		
0.000623	2.305	1.1309
.001861	2.331	1.1258
.003359	2.365	1.1218
.003392	2.362	1.1219
.004057	2.377	1.1202
.004247	2.383	1.1198
Pyridine-Iodine Pentafluoride Complex		
0.000654	2.322	1.1278
.001391	2.355	1.1239
.001775	2.363	1.1254
.003031	2.390	1.1239
.003281	2.415	1.1222
.004877	2.435	1.1204
.007088	2.471	1.1176
Trifluoroacetic Anhydride-Iodine Pentafluoride Complex		
0.000372	2.294	1.1282
.000573	2.306	1.1280
.000641	2.310	1.1271
.000659	2.313	1.1266
.000992	2.331	1.1239
.001777	2.347	1.1219
.003255	2.367	1.1187

TABLE 7, Continued

f_2	ε_{12}	v_{12}
2-Methylpyrazine-Iodine Pentafluoride Complex		
0.000781	2.328	1.1284
.002459	2.369	1.1240
.002704	2.372	1.1222
.002956	2.372	1.1228
.003603	2.400	1.1212
.006653	2.476	1.1139
.012012	2.601	1.1024
2-Fluoropyridine-Iodine Pentafluoride Complex		
0.000398	2.311	1.1293
.000773	2.331	1.1285
.000871	2.333	1.1282
.001585	2.350	1.1268
.002235	2.367	1.1256
.004394	2.463	1.1198
.012044	2.756	1.1011

TABLE 8

DIELECTRIC CONSTANTS AND SPECIFIC VOLUMES OF THE BENZENE SOLUTIONS AT 25° C.

f_2	ε_{12}	v_{12}
	2,6-Dimethylpyridine	
0.002361	2.285	1.1442
.005421	2.299	1.1439
.008902	2.315	1.1439
.011601	2.324	1.1440
.020718	2.361	1.1429
	2-Fluoropyridine	
0.004551	2.338	1.1424
.005176	2.344	1.1424
.008123	2.387	1.1417
.008664	2.392	1.1416
.009957	2.414	1.1411
.017703	2.525	1.1385
.027576	2.664	1.1356
	3-Fluoropyridine	
0.001763	2.285	1.1444
.003974	2.296	1.1437
.007126	2.314	1.1430
.010070	2.331	1.1415
.015000	2.385	1.1398
.018191	2.393	1.1383

TABLE 8, Continued

f_2	ε_{12}	v_{12}
	3-Chloropyridine	
0.005280	2.303	1.1298
.011314	2.338	1.1270
.013519	2.351	1.1263
.016403	2.370	1.1248
.021110	2.396	1.1227
	Pyridine-Iodine Pentafluoride Complex	
0.000654	2.3040	1.1428
.001391	2.3106	1.1423
.001775	2.3421	1.1398
.003031	2.4102	1.1370
.003281	2.3914	1.1365
.004877	2.4158	1.1311
.007088	2.4988	1.1299
	2-Methylpyrazine-Iodine Pentafluoride Complex	
0.0007809	2.301	1.1428
.002459	2.342	1.1382
.002704	2.347	1.1376
.002956	2.352	1.1375
.003603	2.372	1.1356
.006653	2.448	1.1282
.012012	2.559	1.1180

TABLE 8, Continued

f_2	ε_{12}	v_{12}
Trifluoroacetic Anhydride-Iodine Pentafluoride Complex		
0.001605	2.304	1.1400
.002272	2.324	1.1367
.002818	2.360	1.1339
.003715	2.355	1.1259
.004373	2.366	1.1294
.004490	2.371	1.1295
.005062	2.370	1.1273
.005092	2.385	1.1272
.009498	2.481	1.1124
Dioxane-Iodine Pentafluoride Complex		
0.001295	2.299	1.1410
.001782	2.309	1.1389
.002372	2.320	1.1384
.002426	2.322	1.1385
.003452	2.343	1.1358
2-Fluoropyridine-Iodine Pentafluoride Complex		
0.000398	2.310	1.1293
.000773	2.330	1.1285
.000871	2.333	1.1282
.001585	2.349	1.1268
.002235	2.367	1.1256
.004394	2.462	1.1198
.012044	2.756	1.1011

TABLE 9

DIELECTRIC CONSTANTS AND SPECIFIC VOLUMES OF THE CARBON TETRACHLORIDE SOLUTIONS AT 25° C.

f_2	ε_{12}	v_{12}
	2,6-Dimethylpyridine	
0.002478	2.239	0.6318
.003426	2.242	.6323
.004920	2.250	.6327
.009900	2.269	.6342
.010301	2.270	.6343
.019397	2.309	.6370
.022229	2.321	.6379
	2-Fluoropyridine-Iodine Monochloride Complex	
0.001557	2.268	0.6312
.003339	2.402	.6304
.004039	2.326	.6305
.006941	2.424	.6302
.008758	2.485	.6299
.012800	2.610	.6295
	2-Fluoropyridine-Iodine Bromide Complex	
0.000347	2.237	0.6312
.000860	2.248	.6312
.001538	2.270	.6308
.002865	2.319	.6308
.004343	2.370	.6301

TABLE 9, Continued

f_2	ε_{12}	v_{12}
2-Chloropyridine-Iodine Monochloride Complex		
0.000251	2.237	0.6313
.000534	2.256	.6311
.001606	2.315	.6309
.003157	2.401	.6304
.005334	2.517	.6300
2-Chloropyridine-Iodine Bromide Complex		
0.000720	2.249	0.6311
.001679	2.289	.6307
.003028	2.350	.6304
.004700	2.426	.6296
.005696	2.474	.6294
.008748	2.615	.6280
3-Fluoropyridine-Iodine Monochloride Complex		
0.000234	2.238	0.6312
.000407	2.247	.6310
.000918	2.273	.6309
.001370	2.297	.6308
3-Fluoropyridine-Iodine Bromide Complex		
0.000217	2.236	0.6312
.000729	2.254	.6310
.001409	2.284	.6307
.002553	2.326	.6305
.002996	2.344	.6302

TABLE 9, Continued

f_2	ε_{12}	v_{12}
3-Bromopyridine-Iodine Bromide Complex		
0.000270	2.239	0.6314
.000700	2.256	.6311
.001587	2.295	.6305
.002547	2.337	.6300
.003929	2.394	.6298
.005022	2.442	.6286
3-Chloropyridine-Iodine Monochloride Complex		
0.000443	2.249	0.6310
.001153	2.289	.6308
.001456	2.303	.6310
.003480	2.403	.6303
.006070	2.515	.6296
3-Chloropyridine-Iodine Bromide Complex		
0.000758	2.255	0.6309
.001502	2.286	.6307
.002603	2.333	.6304
.003956	2.381	.6297
4-Chloropyridine-Iodine Bromide Complex		
0.000174	2.234	0.6312
.000410	2.242	.6312
.000492	2.247	.6310

TABLE 10

DIELECTRIC CONSTANTS AND SPECIFIC VOLUMES OF THE DIOXANE SOLUTIONS AT 25° C.

f_2	ε_{12}	v_{12}
Dioxane-Iodine Monochloride Complex		
0.000523	2.216	0.9727
.000848	2.226	.9721
.001874	2.250	.9706
.003639	2.288	.9680
.006190	2.348	.9642
.007866	2.448	.9622
.011257	2.463	.9575
Dioxane-Iodine Bromide Complex		
0.001624	2.222	0.9706
.002333	2.236	.9692
.003434	2.244	.9676
.004958	2.261	.9653
.006899	2.285	.9624
.010582	2.321	.9565
.015201	2.374	.9492

TABLE 11

DIELECTRIC CONSTANTS AND SPECIFIC VOLUMES OF THE BENZENE SOLUTIONS AT 35° C.

f_2	ε_{12}	v_{12}
Dioxane-Iodine Pentafluoride Complex		
0.000104	2.271	1.1556
.002397	2.299	1.1526
.004619	2.340	1.1471
.005080	2.347	1.1492
.010310	2.444	1.1380

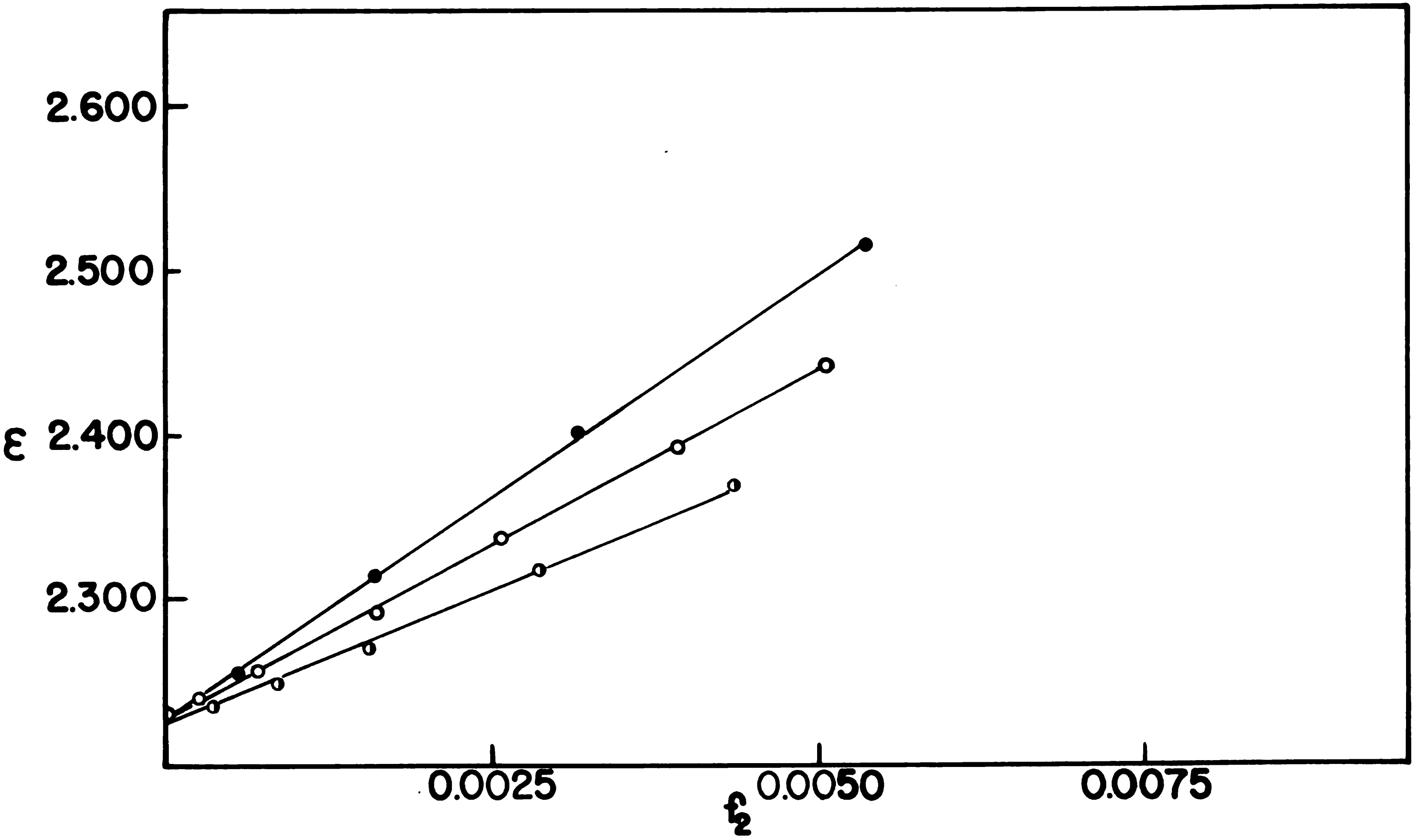


Figure 7. Dielectric constants as a function of mole fraction solute for carbon tetrachloride solutions of ● 2-Chloropyridine.ICl, ○ 3-Bromopyridine.IBr, and ◐ 2-Fluoropyridine.IBr.

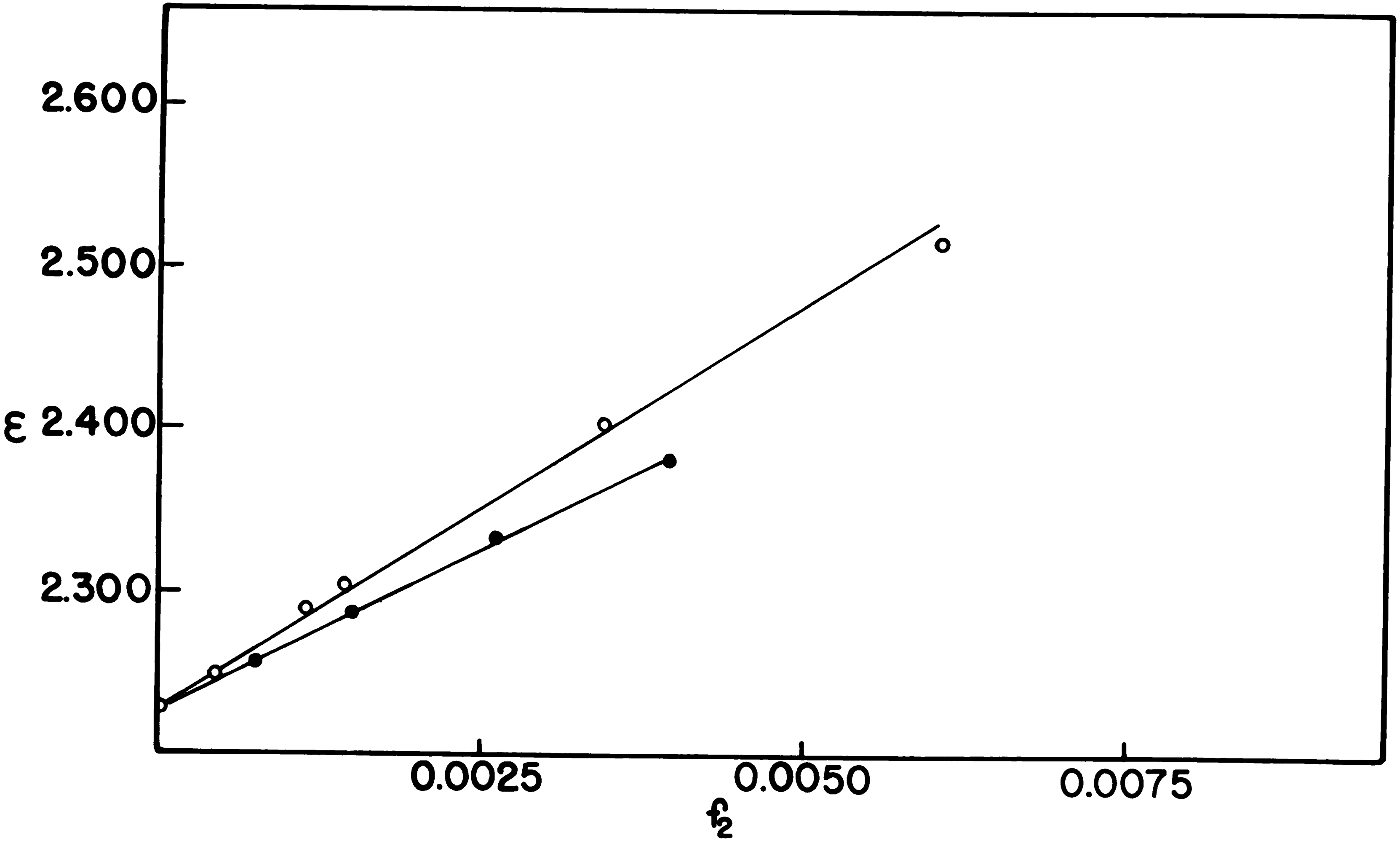


Figure 3. Dielectric constants as a function of mole fraction solute for carbon tetrachloride solutions of ○ 3-chloropyridine.ICl and ● 3-chloropyridine.IBr.

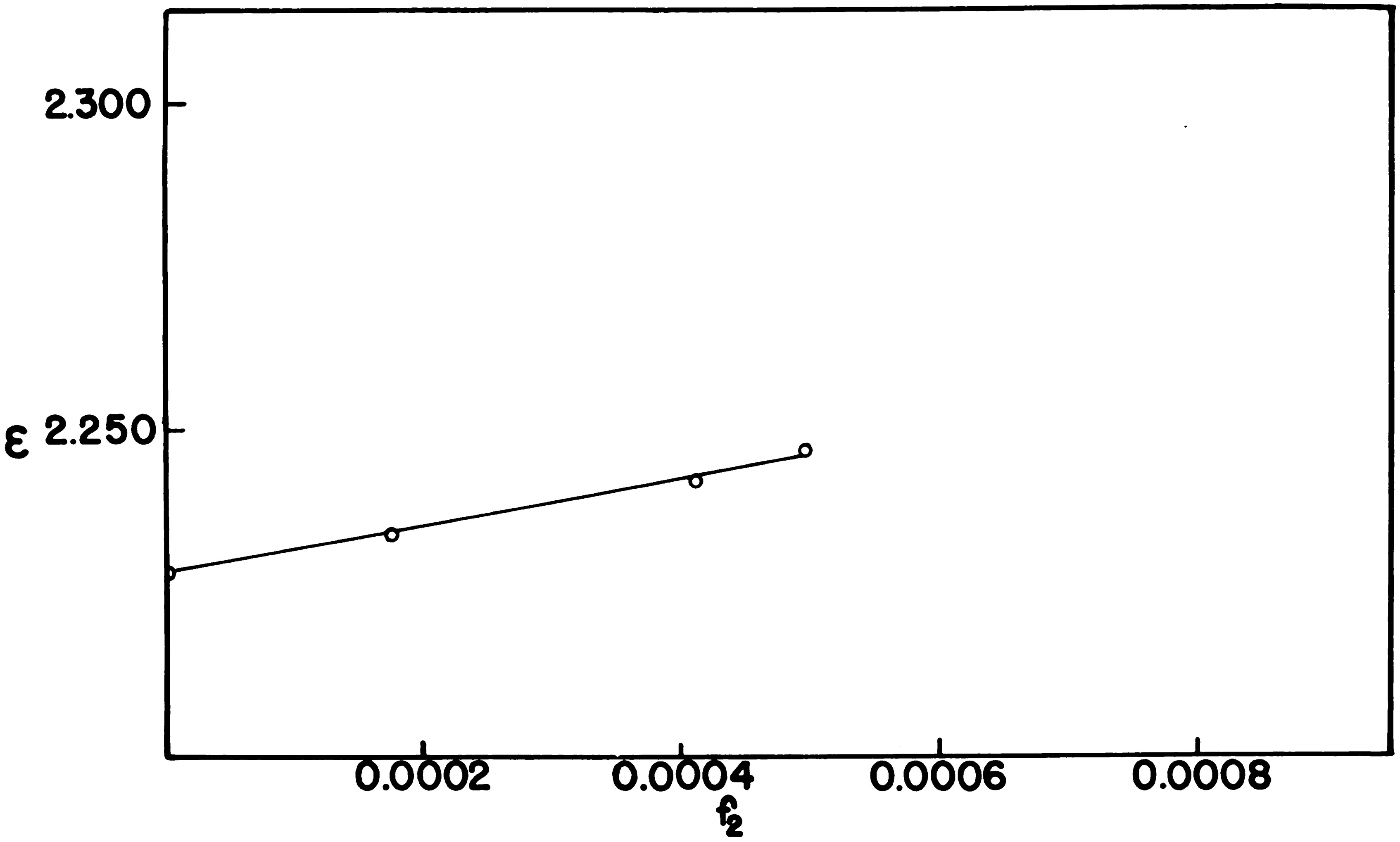


Figure 9. Dielectric constant as a function of mole fraction solute for carbon tetrachloride solution of o 4-chloropyridine.ICl.

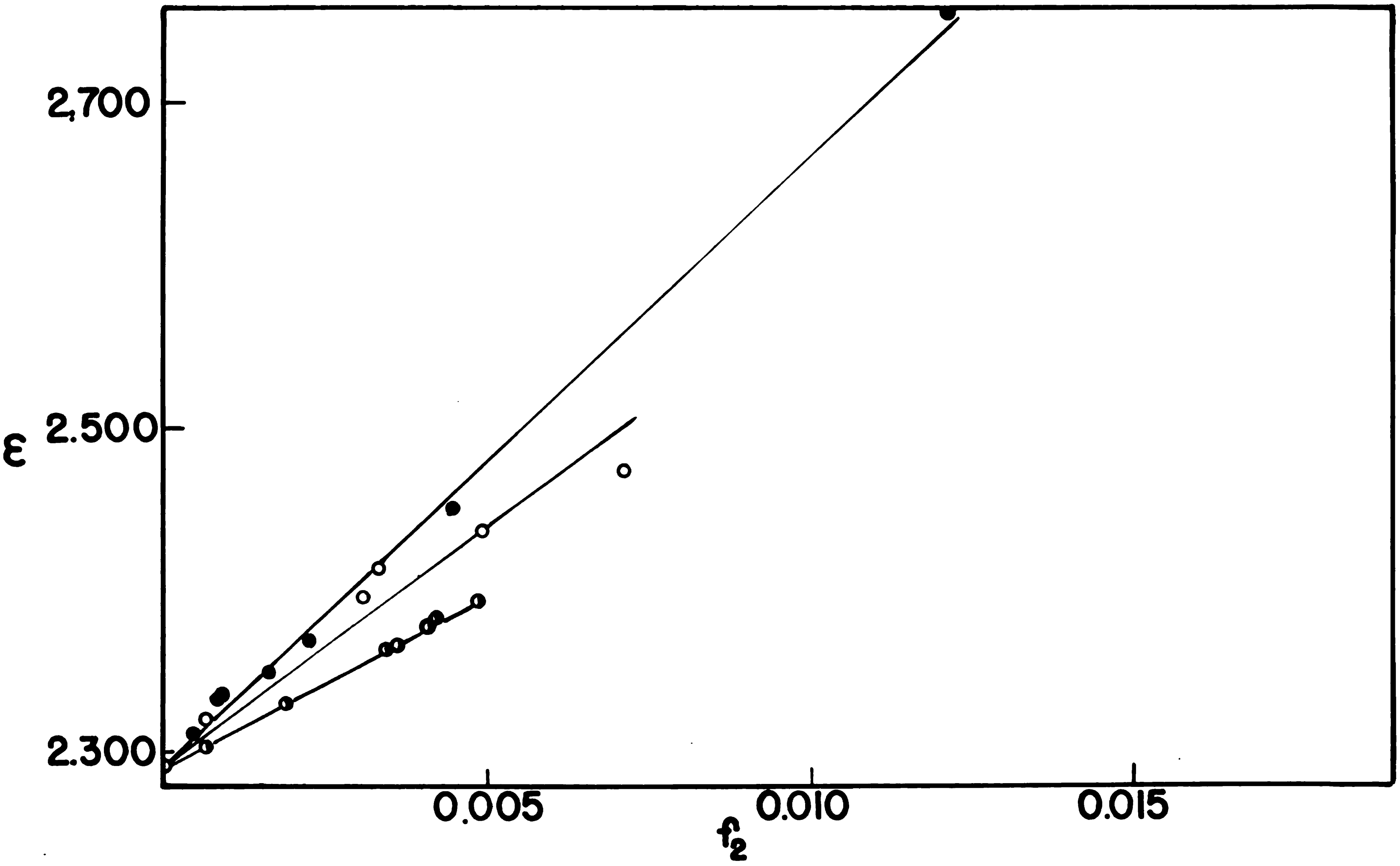


Figure 10. Dielectric constant as a function of mole fraction solute for benzene solutions of ● 2-fluoropyridine.IF_5, ○ pyridine.IF_5 and ○ dioxane.IF_5.

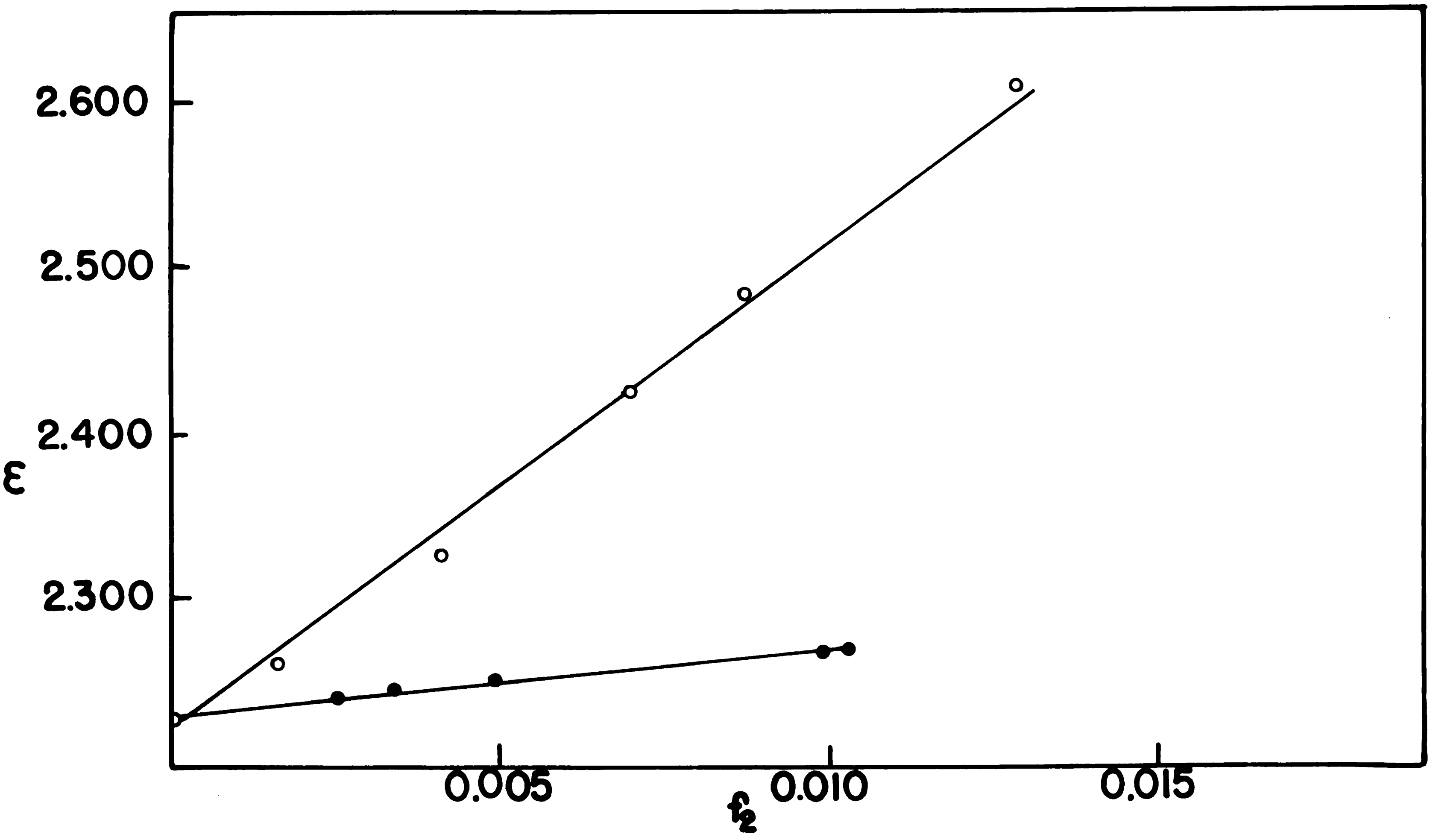


Figure 11. Dielectric constants as a function of mole fraction solute for carbon tetrachloride solutions of ○ 2-fluoropyridine.ICl and ● 2,6-dimethylpyridine.

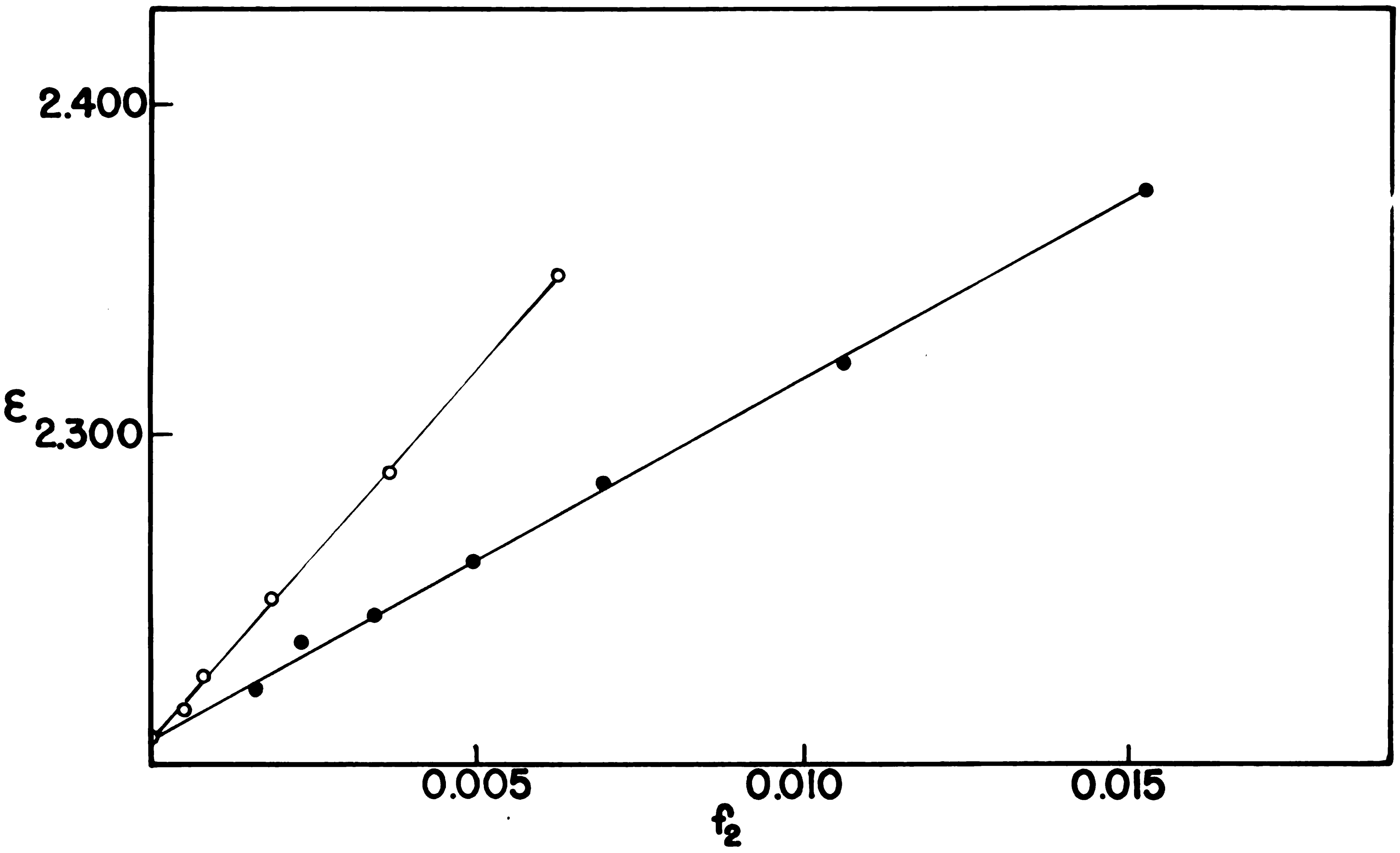


Figure 12. Dielectric constants as a function of mole fraction solute for dioxane solutions of ○ dioxane.ICl and ● dioxane.IBr.

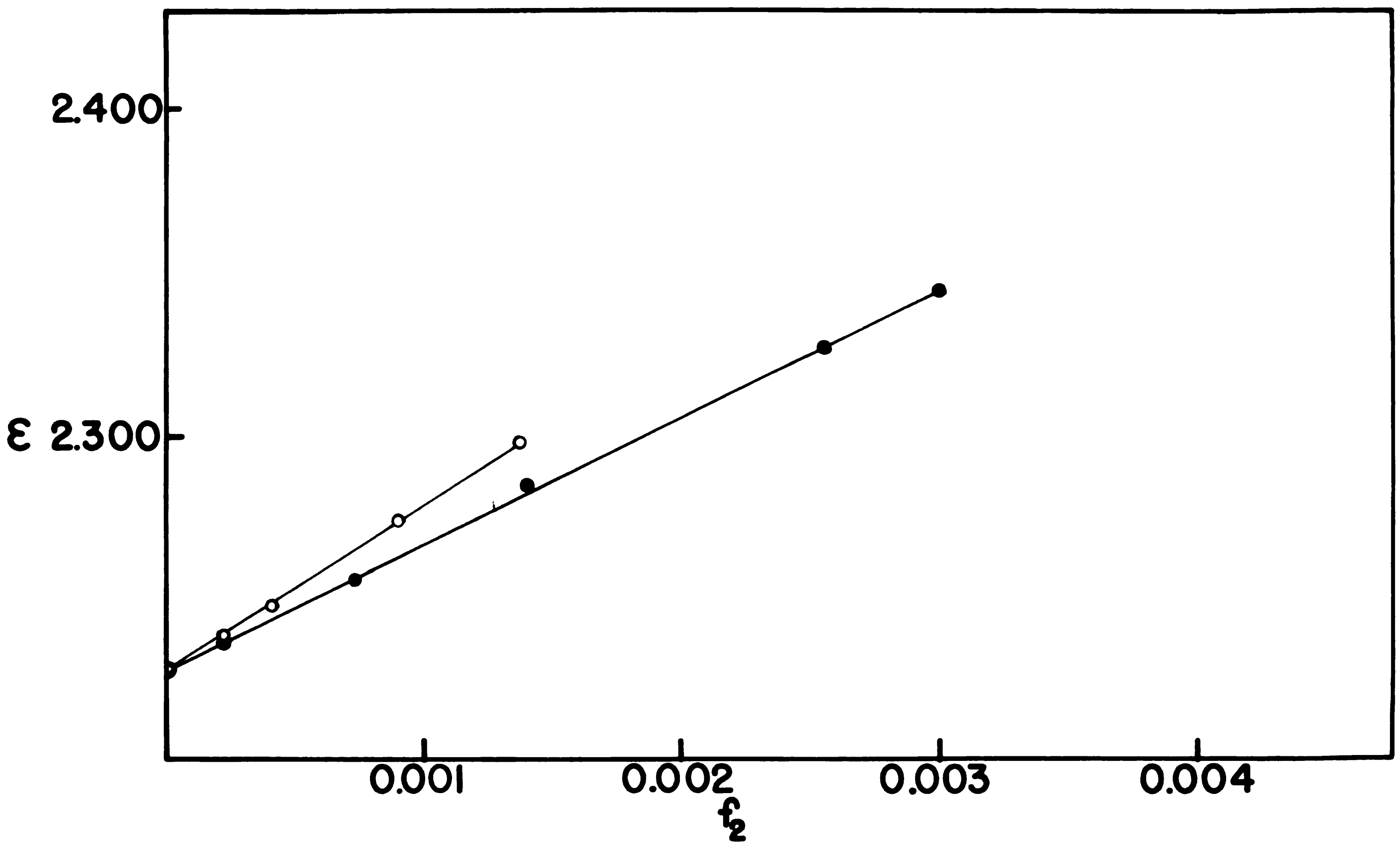


Figure 13. Dielectric constants as a function of mole fraction solute for carbon tetrachloride solutions of ○ 3-fluoropyridine.ICl and ● 3-fluoropyridine.IBr.

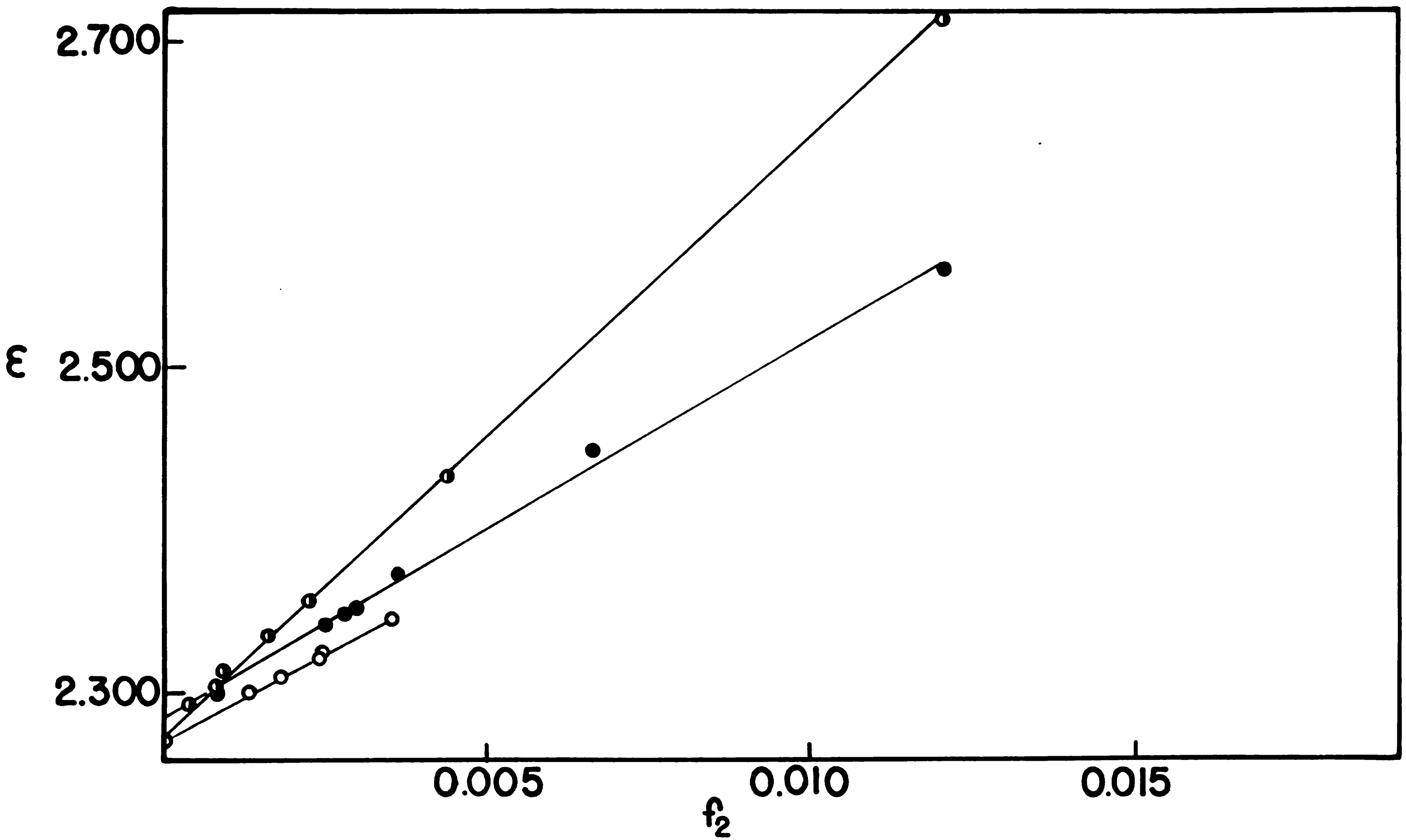


Figure 14. Dielectric constants as a function of mole fraction solute for benzene solutions of ◐ 2-fluoropyridine.IF_5, ○ dioxane.IF_5 and ● 2-methylpyrazine.IF_5.

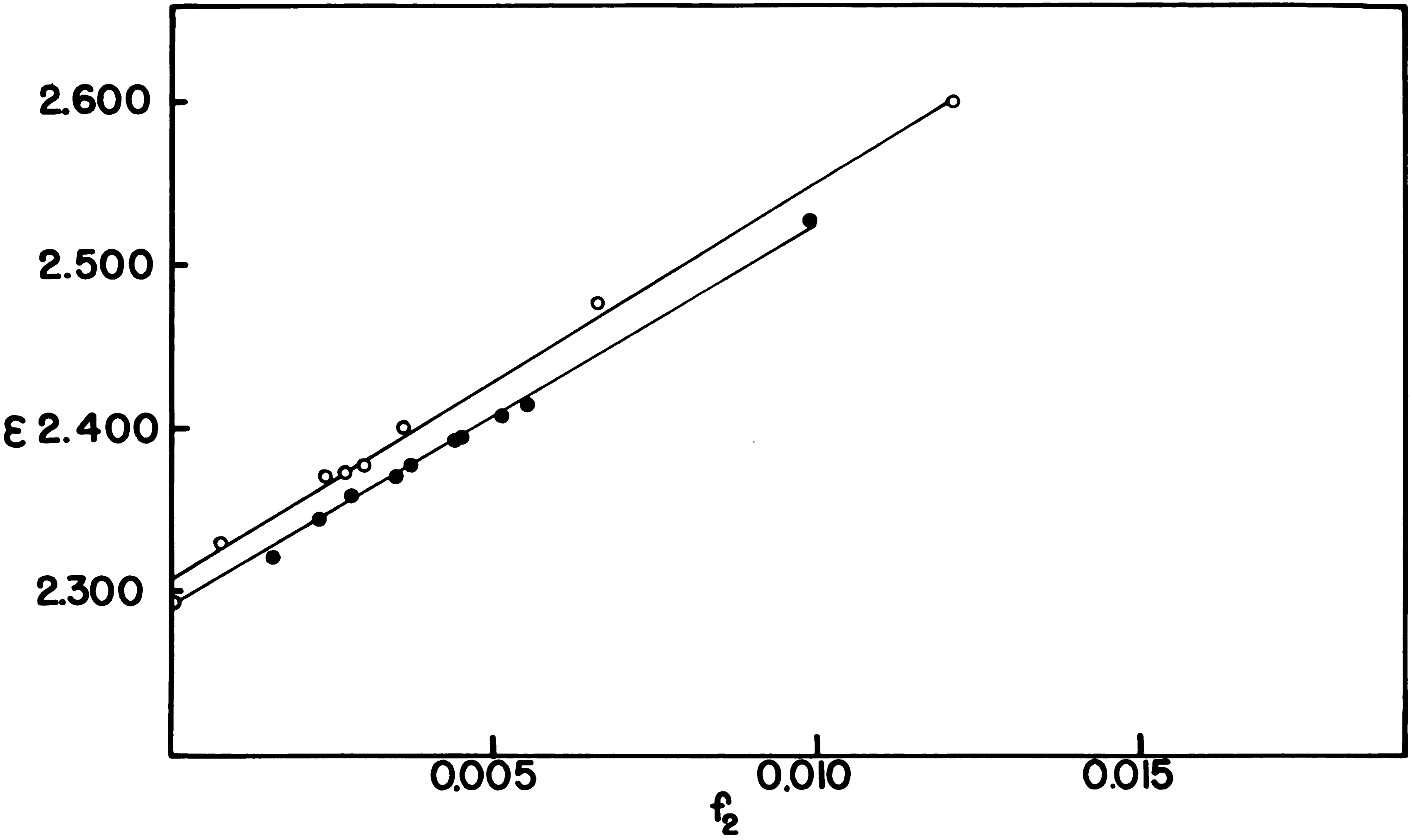


Figure 15. Dielectric constants as a function of mole fraction solute for benzene solutions of ○ 2-methylpyrazine.IF_5 and ● trifluoroacetic anhydride.IF_5.

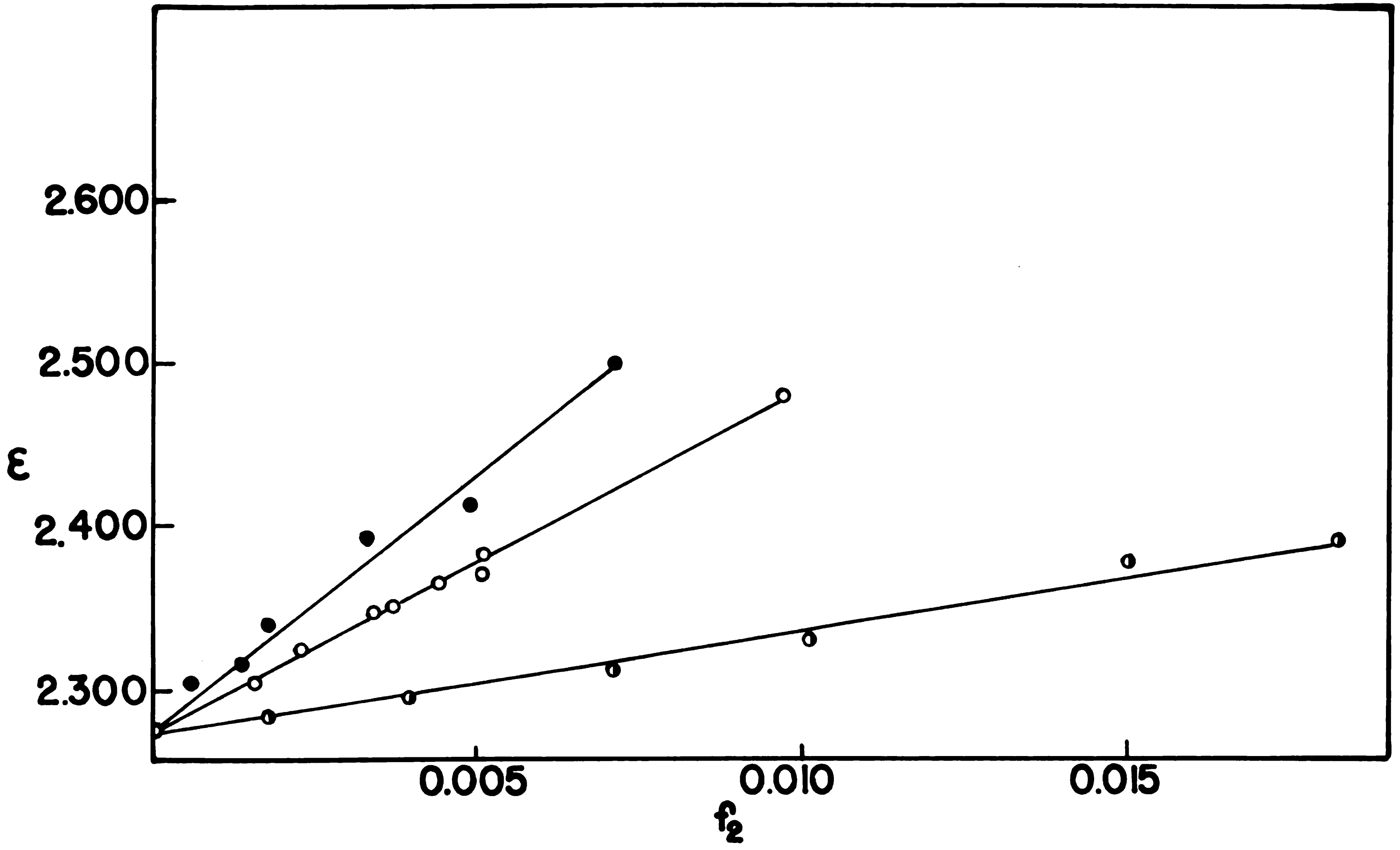


Figure 16. Dielectric constants as a function of mole fraction solute for benzene solutions of ● pyridine.IF_5, ○ trifluoroacetic anhydride.IF_5 and o 3-fluoropyridine.

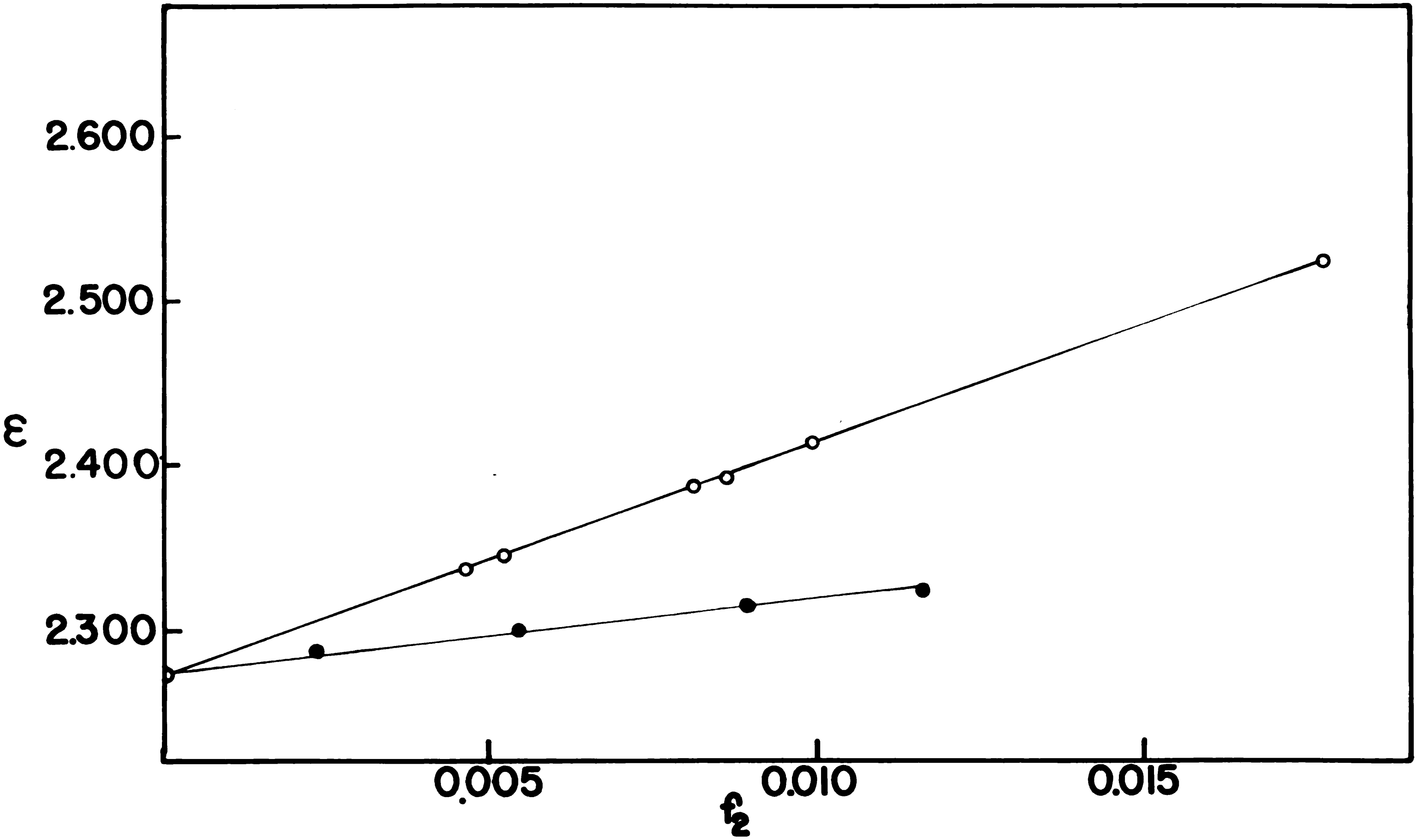


Figure 17. Dielectric constants as a function of mole fraction solute for benzene solutions of ○ 2-fluoropyridine and ● 2,6-dimethylpyridine.

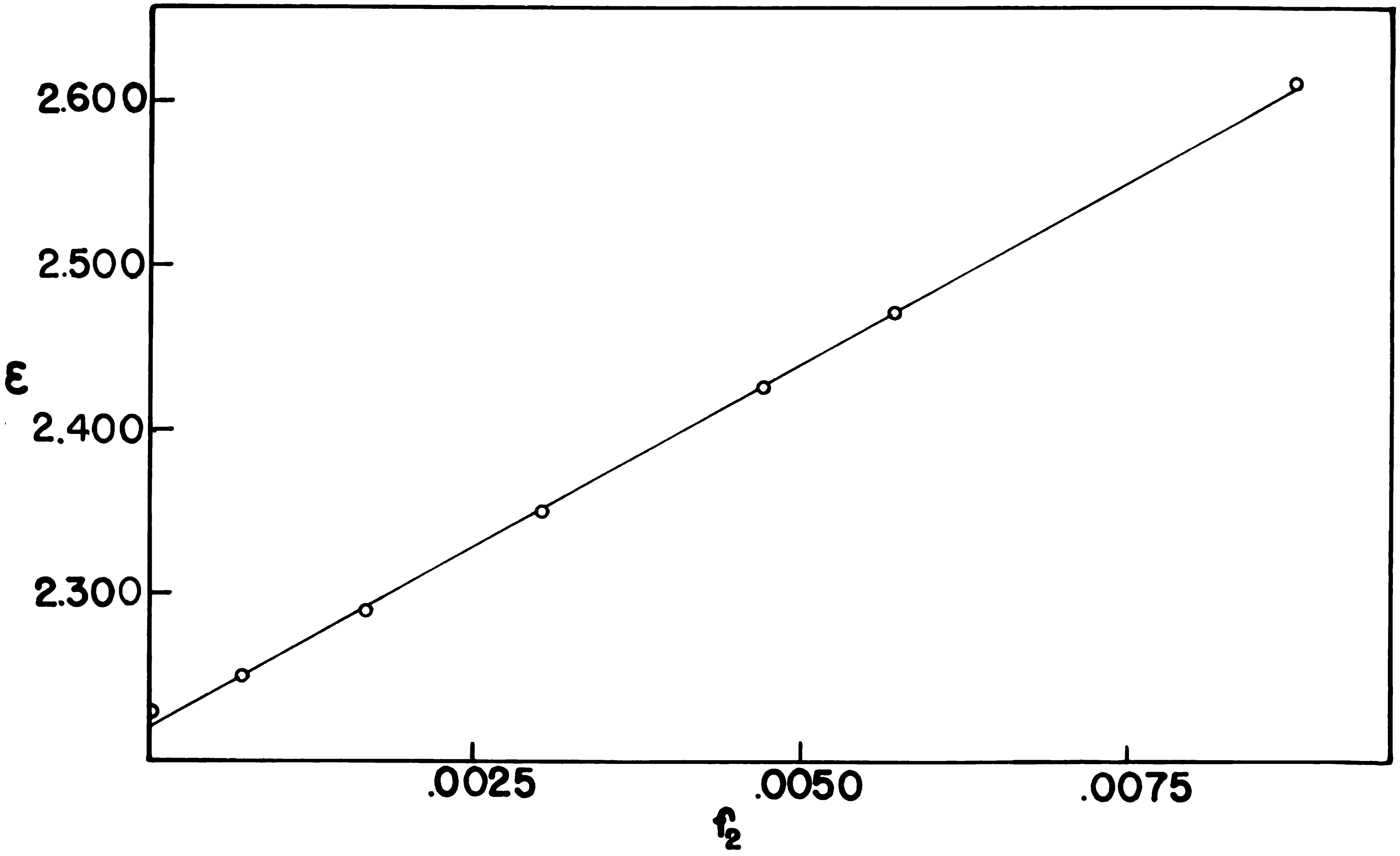


Figure 15. Dielectric constants as a function of mole fraction solute for carbon tetrachloride solution of o 3-chloropyridine.ICl.

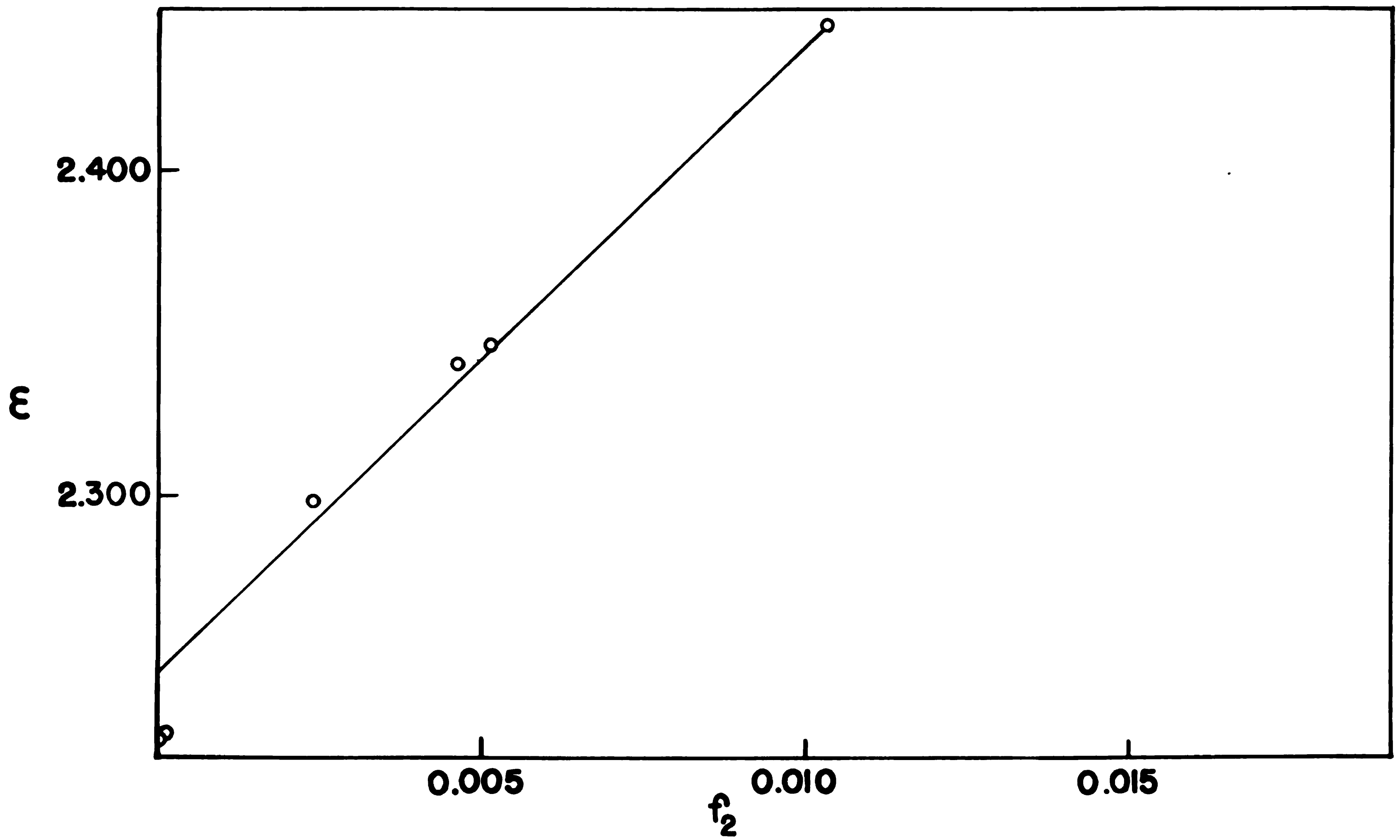


Figure 19. Dielectric constants as a function of mole fraction solute for benzene solution of ○ dioxane.IF_5.

TABLE 12

DIPOLE MOMENTS, MOLAR POLARIZATIONS, MOLAR REFRACTIONS AND EMPIRICAL CONSTANTS FOR MOLECULAR COMPLEXES

Solvent	T.°C.	α'	β'	P_2^{∞}	MR_D	μ
2,6-Dimethylpyridine						
CCl_4	25°	4.16	0.324	101.87	33.31	1.83
2,6-Dimethylpyridine						
C_6H_6	25°	4.69	-0.095	100.28	33.31	1.81
2-Fluoropyridine						
C_6H_6	25°	15.61	-0.144	259.24	23.85	3.39
3-Fluoropyridine						
C_6H_6	25°	5.67	-0.315	109.11	23.85	2.04
3-Chloropyridine						
C_6H_6	25°	5.86	-0.948	102.81	28.88	1.90
Pyridine-Iodine Pentafluoride						
C_6H_6	15°	24.55	-1.713	415.05	43.24	4.19
	25°	30.99	-2.246	505.71	43.24	4.56
2-Fluoropyridine-Iodine Monochloride						
CCl_4	25°	30.35	-0.127	535.87	43.65	4.90
2-Fluoropyridine-Iodine Bromide						
CCl_4	25°	33.26	-0.278	585.07	46.55	5.13

TABLE 12, continued

Solvent	T.°C.	α'	β'	P_2^{∞}	MR_D	μ
2-Fluoropyridine-Iodine Pentafluoride						
C_6H_6	15°	38.24	-2.432	601.04	42.95	5.13
	25°	35.93	-2.486	578.84	42.95	5.12
2-Chloropyridine-Iodine Monochloride						
CCl_4	25°	54.36	-0.236	926.04	48.68	6.55
2-Chloropyridine-Iodine Bromide						
CCl_4	25°	44.85	-0.374	773.03	51.58	5.94
3-Fluoropyridine-Iodine Monochloride						
CCl_4	25°	51.14	-0.258	869.56	43.65	6.35
3-Fluoropyridine-Iodine Bromide						
CCl_4	25°	38.79	0.335	672.98	46.55	5.53
3-Chloropyridine-Iodine Monochloride						
CCl_4	25°	50.40	-0.194	863.38	48.68	6.31
3-Chloropyridine-Iodine Bromide						
CCl_4	25°	40.39	-0.330	702.29	51.58	5.64
3-Bromopyridine-Iodine Bromide						
CCl_4	25°	42.66	-0.500	739.85	54.48	5.79

TABLE 12, continued

Solvent	T.°C.	α'	β'	P_2^{∞}	MR_D	μ
			Dioxane-Iodine Monochloride			
$C_4H_8O_2$	25°	22.83	-1.420	365.87	41.92	3.98
			Dioxane-Iodine Bromide			
$C_4H_8O_2$	25°	10.95	-1.567	201.89	44.82	2.77
			Dioxane-Iodine Pentafluoride			
C_6H_6	15°	20.75	-2.870	336.66	40.85	3.73
	25°	20.06	-2.650	338.54	40.85	3.81
	35°	18.51	-1.980	338.08	40.85	3.87
			Trifluoroacetic Anhydride-Iodine Pentafluoride			
C_6H_6	15°	22.54	-3.310	393.18	40.89	4.08
	25°	21.15	-3.320	379.99	40.89	4.07
			2-Methylpyrazine-Iodine Pentafluoride			
C_6H_6	15°	26.81	-2.560	433.15	49.16	4.26
	25°	25.95	-2.530	433.79	49.16	4.33

TABLE 13

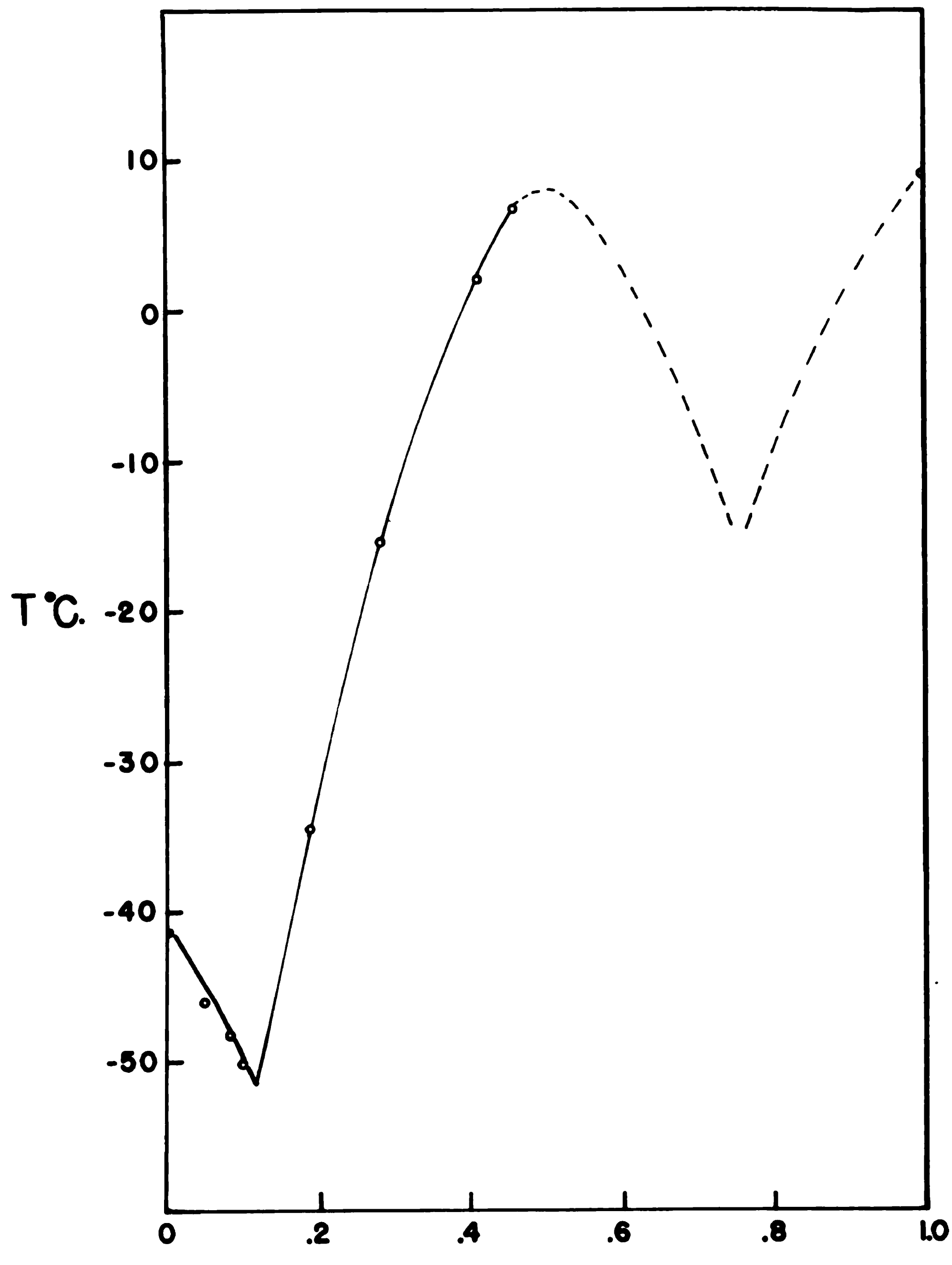
CRYOSCOPIC DATA FOR PYRIDINE-IODINE PENTAFLUORIDE SOLUTIONS

Weight C_5H_5N (gm.)	Weight IF_5 (gm.)	Mole Percent IF_5	F.P. °C.
2.1310	0.000	00.00	-41.34
2.1310	.315	5.00	-46.67
1.5702	.385	8.41	-47.84
2.1310	.622	9.41	-50.12
1.5702	1.055	19.31	-34.69
1.5702	1.755	28.47	-15.38
1.5702	3.108	41.36	2.13
1.5702	3.778	46.33	6.83
		100.00	9.60

TABLE 14

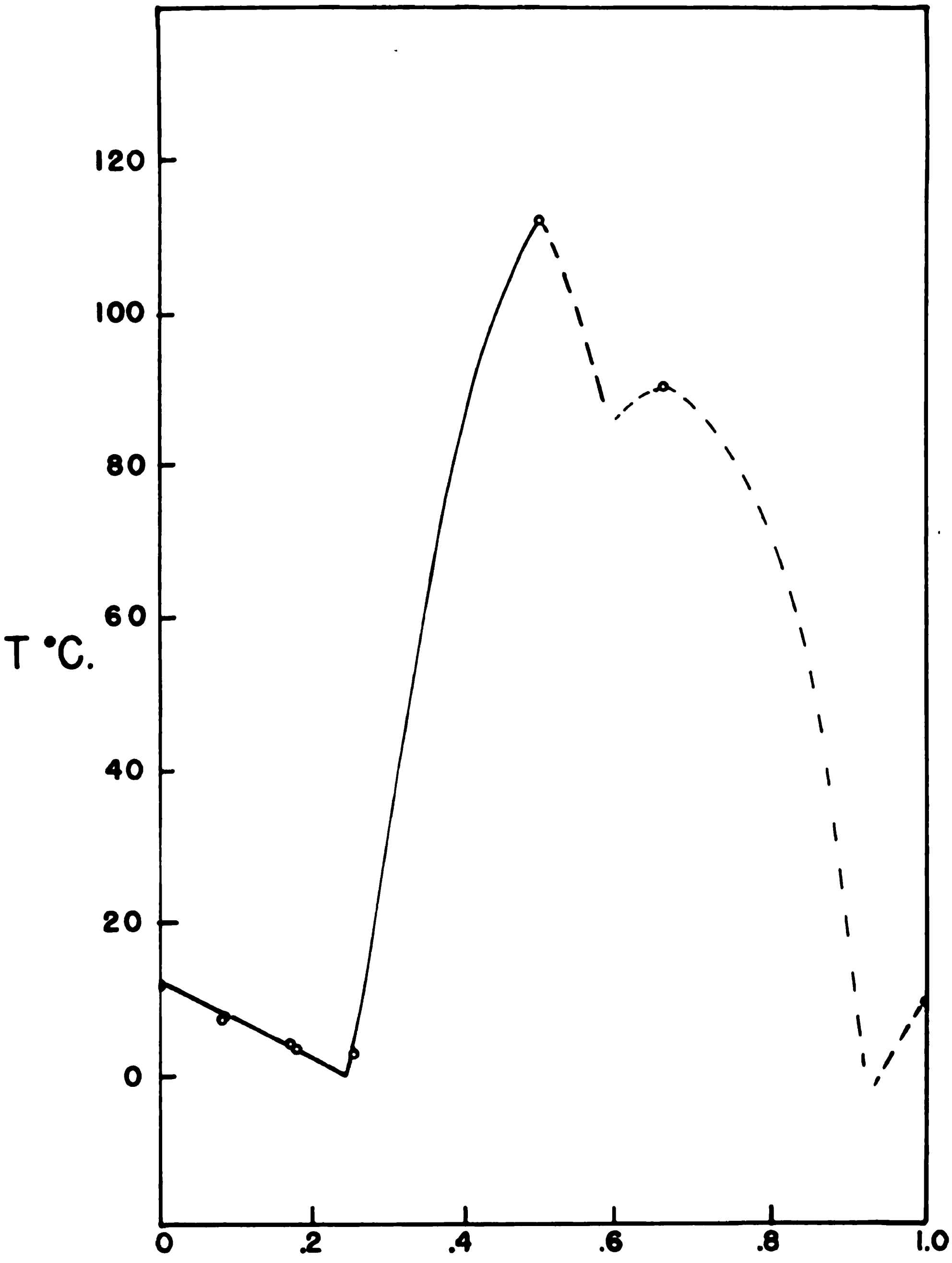
CRYOSCIPIC DATA FOR DIOXANE-IODINE PENTAFLUORIDE SOLUTIONS

Weight $C_4H_8O_2$(gm.)	Weight IF_5(gm.)	Mole Percent IF_5	F.P. °C.
4.8991	0.000	0.00	11.66
4.8991	1.125	8.34	6.57
2.7009	.632	8.48	6.97
2.7009	1.410	17.18	3.41
4.8991	2.708	18.04	3.12
2.7009	2.318	25.31	2.86
1-1 Ratio Compound		50.00	112.00
1-2 Ratio Compound		66.67	90.00
		100.00	9.60



MOLE FRACTION OF IODINE PENTAFLUORIDE

Figure 20. Phase diagram of the system pyridine-iodine pentafluoride: Author's conception of the remaining portion of the diagram shown by dotted lines.



MOLE FRACTION OF IODINE PENTAFLUORIDE

Figure 21. Phase diagram of the system dioxane-iodine pentafluoride: Author's conception of the remaining portion of the diagram shown by dotted lines.

TABLE 15

ULTRAVIOLET ABSORPTION SPECTRA OF THE AMINE-HALOGEN COMPLEXES

Complex	Wave Length of Abs. Max. mμ	a_c[1]	Isosbestic Point mμ
2-Chloropyridine.ICl	336	217	396
3-Chloropyridine.ICl	302	727	392
4-Chloropyridine.ICl	300	604	389
2-Fluoropyridine.ICl	335	246	397
2-Fluoropyridine.I_2	440	700	484

TABLE 16

EQUILIBRIUM CONSTANTS OF AMINE-HALOGEN COMPLEXES IN CARBON TETRACHLORIDE AT 25° C.

Complex	Equil. Const.[2]
2-Chloropyridine.ICl	2.0×10^{-4}
3-Chloropyridine.ICl	1.2×10^{-5}
4-Chloropyridine.ICl	4.8×10^{-7}
2-Fluoropyridine.ICl	1.7×10^{-4}
2-Fluoropyridine.I_2	1

[1] Molar absorbancy index or extinction coefficient.

[2] See Equation 27.

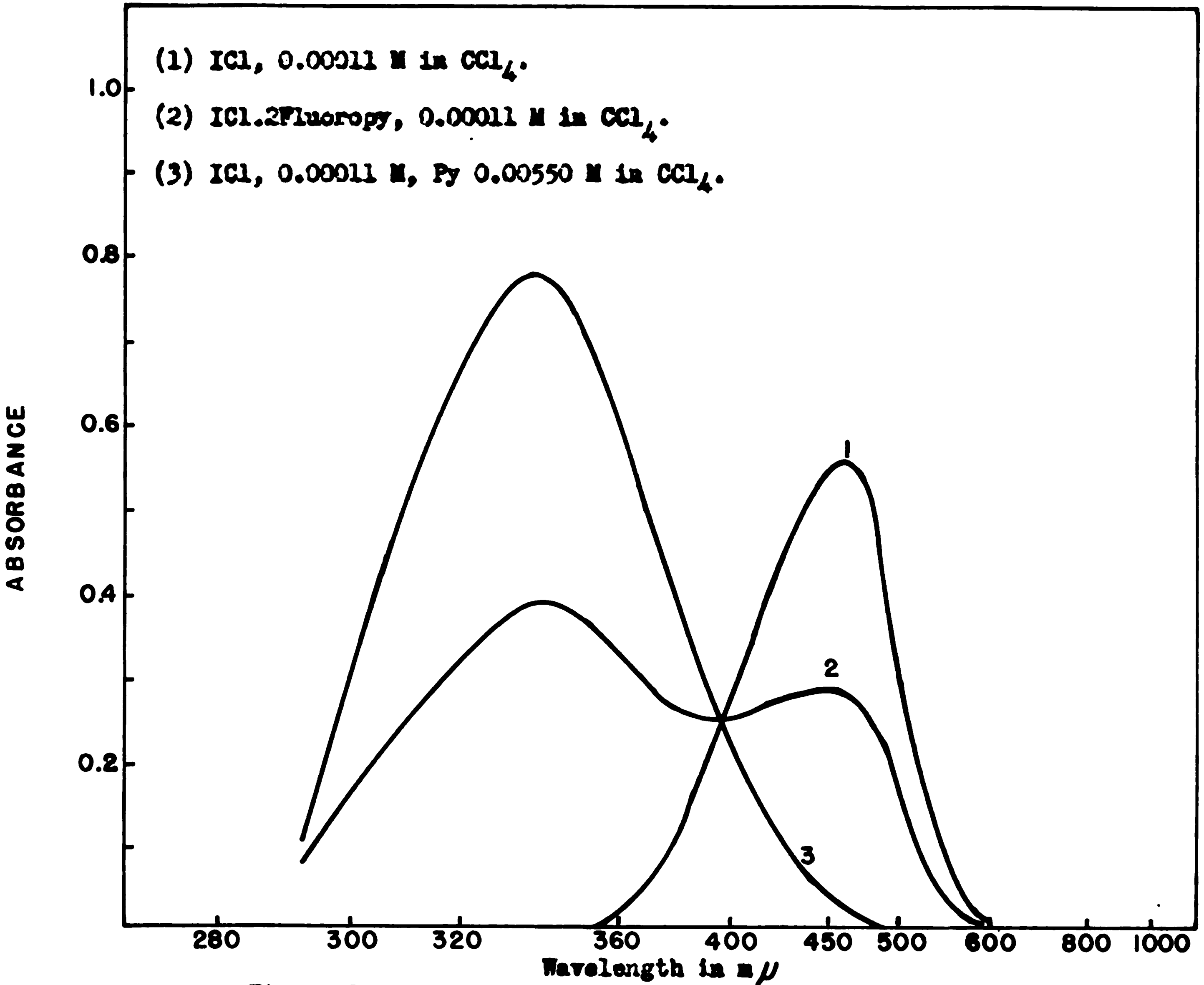


Figure 22. Absorption spectra of carbon tetrachloride solutions containing a constant concentration (0.00011 M) of ICl and varying amounts of 2-fluoropyridine.

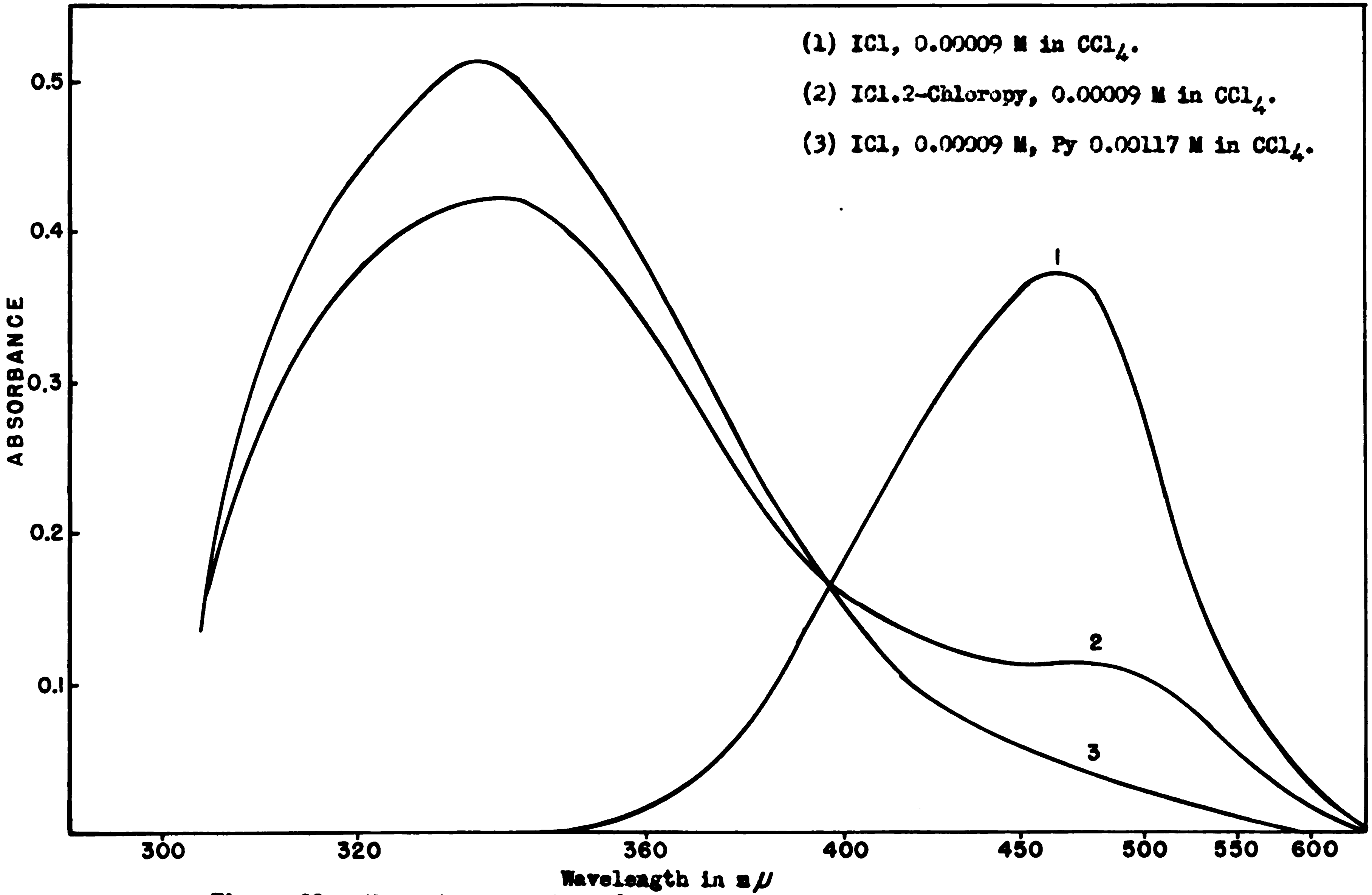


Figure 23. Absorption spectra of carbon tetrachloride solutions containing a constant concentration (0.00009 M) of ICl and varying amounts of 2-chloropyridine.

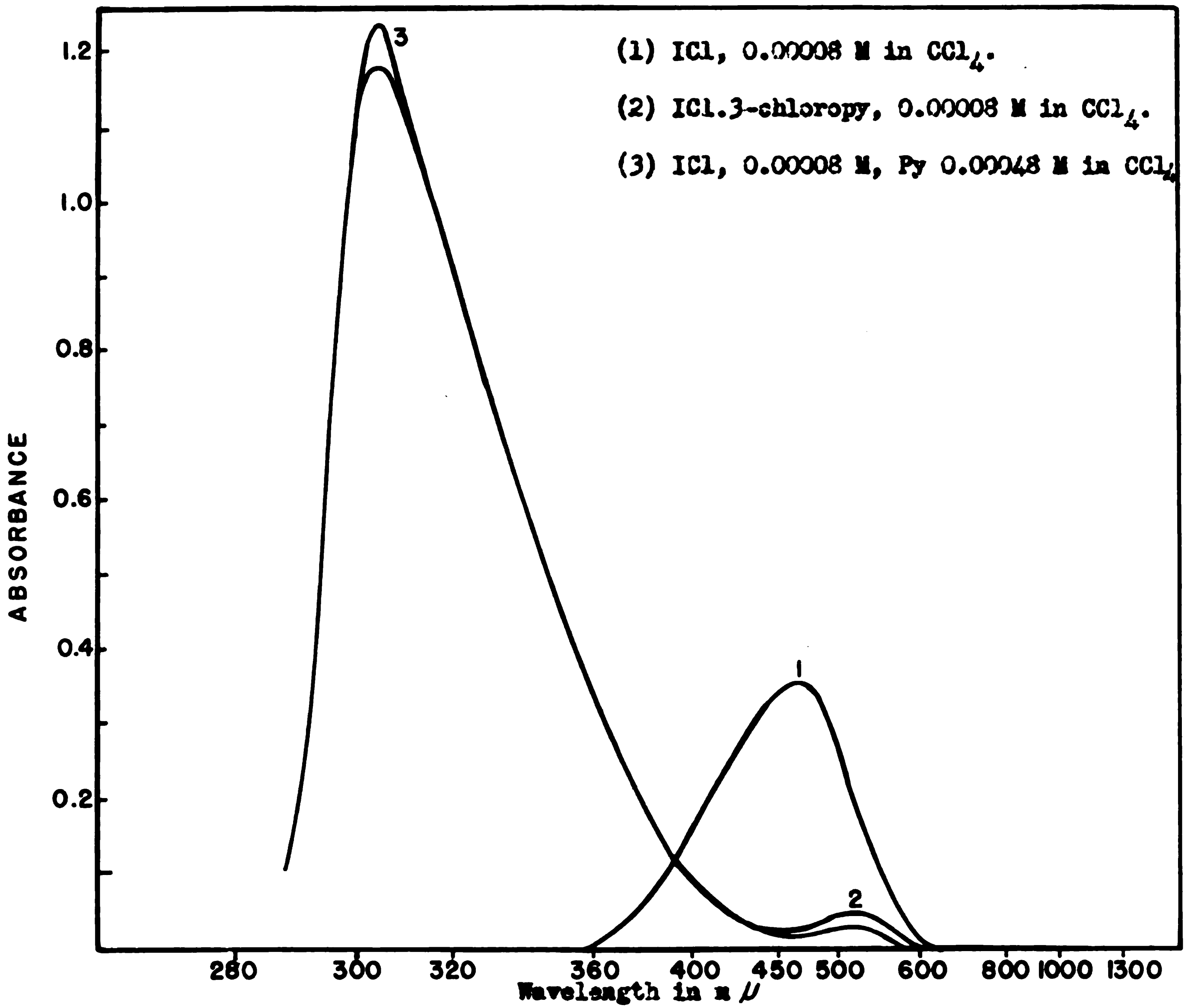


Figure 24. Absorption spectra of carbon tetrachloride solutions containing a constant concentration (0.00008 M) of ICl and varying amounts of 3-chloropyridine.

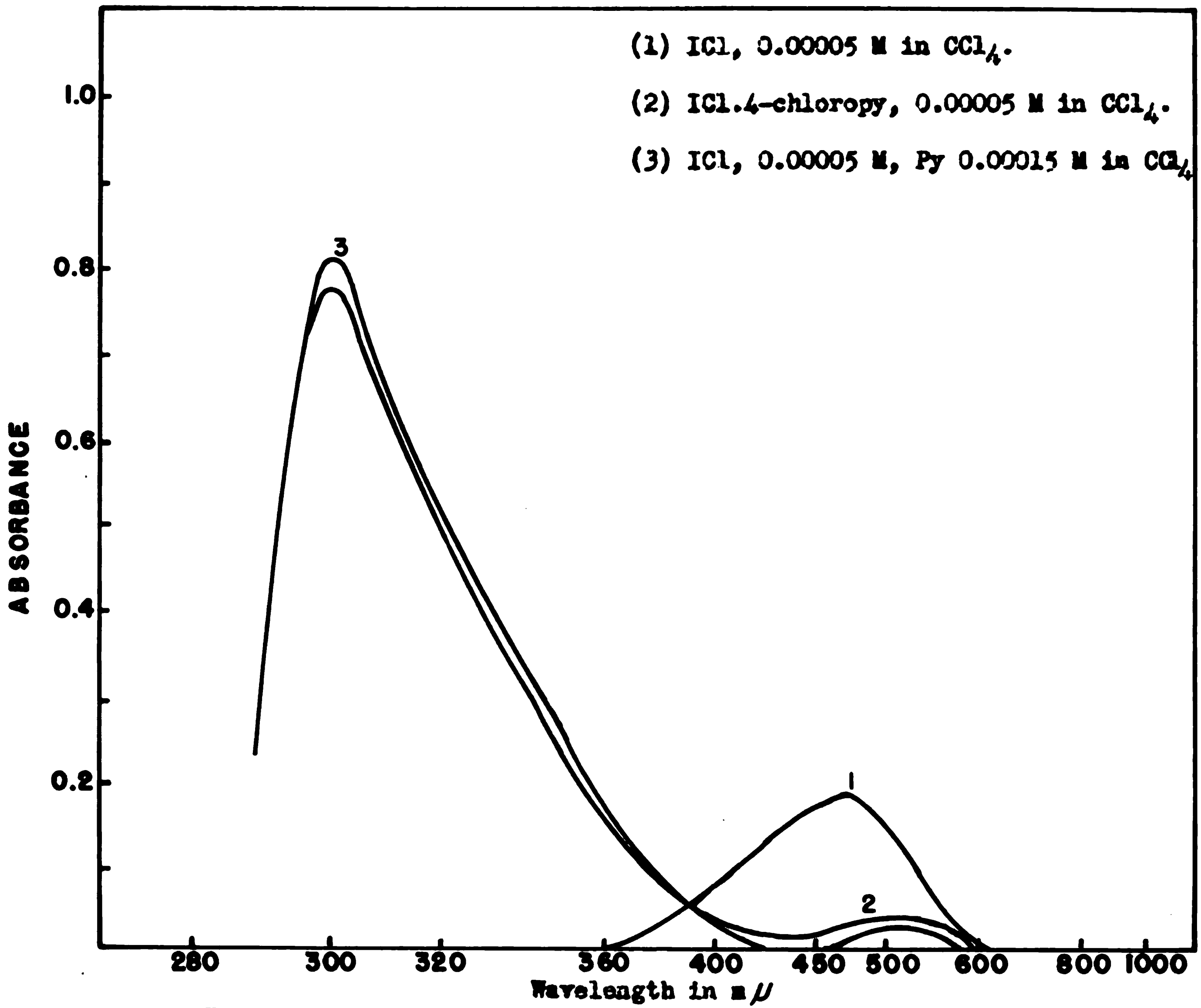


Figure 25. Absorption spectra of carbon tetrachloride solutions containing a constant concentration (0.00005 M) of ICl and varying amounts of 4-chloropyridine.

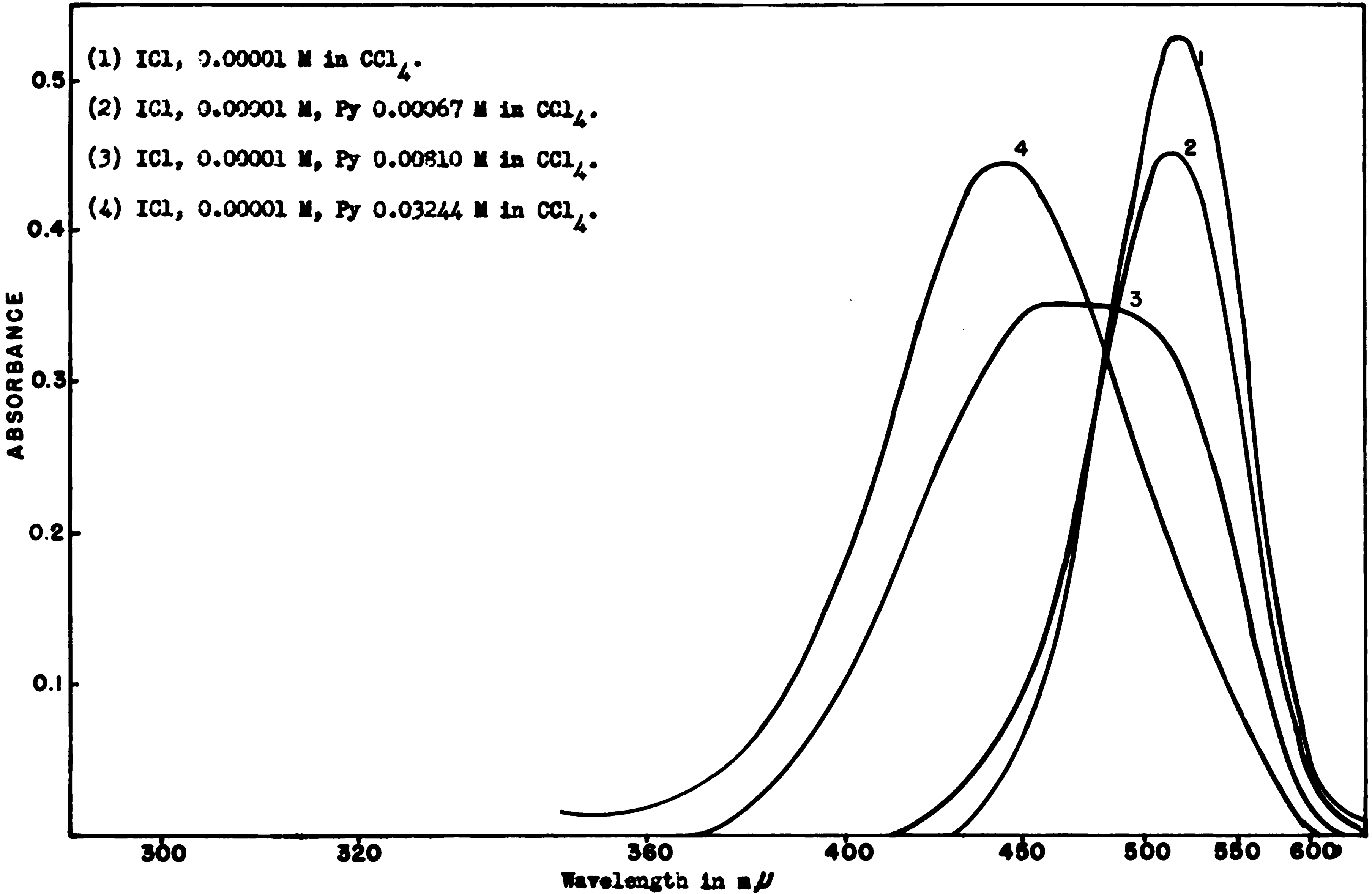


Figure 26. Absorption spectra of carbon tetrachloride solutions containing a constant concentration (0.00001 M) ICl and varying amounts of 2-fluoropyridine.

DISCUSSION

Phase Diagram Studies

The phase diagram of the pyridine-iodine pentafluoride system (Figure 20) is that of a two-component system with compound formation at 0.5 mole fraction iodine pentafluoride. The first eutectic point is at 0.115 mole fraction iodine pentafluoride. The 1:1 compound has a melting point of about 9° C. It is not a very stable compound as indicated by the change of slope of the freezing point curve at the maximum.

The phase diagram of the dioxane-iodine pentafluoride system (Figure 21) appears to be that of a two-component system with two compounds formed at 0.5 and 0.66 mole fraction iodine pentafluoride. The first eutectic point is at 0.245 mole fraction iodine pentafluoride. The 1:2 compound may exhibit a true maximum or it may show only a peritectic point. It exhibited its instability by dissociating into the 1:1 compound and iodine pentafluoride when dried at reduced pressure.

Dipole Moments

The observed and calculated dipole moments of the molecular complexes are listed in Table 17. The calculation of the dipole moment of a complex containing two group moments m_1 and m_2, in fixed positions was made by use of the following

TABLE 17

OBSERVED AND CALCULATED DIPOLE MOMENTS OF MOLECULAR COMPLEXES

Complex	Observed	Calculated	% Charge Shift[1]
2-Fluoropyridine.ICl	4.90	4.64	2
3-Fluoropyridine.ICl	6.35	3.42	27
2-Chloropyridine.ICl	6.55	4.68	17
3-Chloropyridine.ICl	6.31	3.43	26
Dioxane.ICl	3.98	1.49	20
2-Fluoropyridine.IBr	5.13	4.36	7
3-Fluoropyridine.IBr	5.53	3.14	22
2-Chloropyridine.IBr	5.94	4.40	14
3-Chloropyridine.IBr	5.64	3.15	23
4-Chloropyridine.IBr	5.79	3.13	24
Dioxane.IBr	1.65	1.21	4
Pyridine.IF_5	4.56	4.23	3
2-Fluoropyridine.IF_5	5.12	5.15	0
2-Methylpyrazine.IF_5	4.33	2.11	20
Dioxane.IF_5	3.81	2.18	13
Trifluoroacetic anhydride.IF_5	4.07		

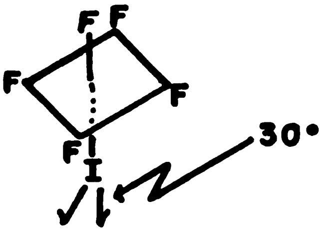
---

[1] See text for explanation.

equation:

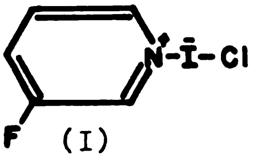
$$\mu = (m_1^2 + m_2^2 + 2m_1m_2 \cos \theta)^{1/2} \qquad (28)$$

where θ is the angle between the fixed moments. The iodine monochloride and iodine bromide complexes were assumed to be linear. The iodine pentafluoride complexes were assumed to be at an angle of 30° with respect to the other moment.

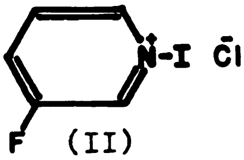


The increases in the **observed** dipole moments of the complexes over the calculated moments is due to shift of electrons between either the nitrogen or oxygen atom and the iodine atom.

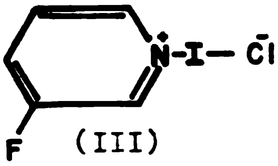
Possible structures of 3-fluoropyridine.ICl that could contribute to this increase in dipole moment are:



(I)



(II)



(III)

The "inner" complex of Mulliken (35) could also contribute to the dipole moment.

Of these various structures, the inner complex can be eliminated. Mulliken and Reed (36) state that in the polar solvent pyridine, the pyridine-iodine complex has little tendency to form an inner complex. In a nonpolar solvent the tendency should be even smaller. Structure II can also be eliminated as the principal structure contributing to the dipole moment. From spectrophotometric studies there is only a single absorption band in the ultraviolet region above 290 m . This band must correspond to the complex in either structure I or III since it corresponds to the I-Cl absorption band.

In structure III, the bond between the iodine and chlorine atoms would be lengthened from its normal covalent distance of 2.32 Å. and the bond between the nitrogen and iodine atoms would be shorter than the normal covalent distance of 2.07 Å. Hassel (19, 20, 21) has measured bond distances in the following complexes in the solid state: pyridine.ICl, dioxane.2ICl, dioxane.Br_2, trimethylamine.ICl and trimethylamine.I_2. He has found that the halogen-halogen bond distance is the same or only slightly longer than the normal covalent bond distance, while the oxygen-halogen or nitrogen-halogen bond distance is considerably longer than the covalent bond distance.

The preceding evidence strongly indicates that structure I is the predominant structure for the complex. On this basis, then, it is possible to calculate the amount of electronic charge shift from the nitrogen atom to the iodine atom that would account for the increase in the dipole moment.

The difference between the observed and calculated dipole moments for 3-fluoropyridine.ICl is 2.93 D. Assuming that the N-I distance in 3-fluoropyridine.ICl is 2.30 Å. as measured by Hassel (19), this increased moment corresponds to an electronic charge shift of 27%.

The electronic charge shift for the remaining complexes have been calculated assuming N-I and O-I bond distances of 2.30 Å. and 2.60 Å., respectively, and are listed in the right hand column of Table 17.

The smaller extent of charge transfer for the pyridines substituted in the two position may be due to two factors. The substituent in the two position may sterically hinder the group on the nitrogen. This could cause the two dipoles of the complex to be at an angle rather than linear as assumed in the calculation. The second factor could be that the substituent groups are electron withdrawing. They could reduce the availability of the unshared pair of electrons on the nitrogen for complex formation. The decrease in the percent of charge shift in going from the chloro to the fluoro substituted complexes can be accounted for by the increase in electronegativity of the halogen. This same trend is noticed in the iodine bromide complexes with pyridine substituted in the three position where the percent charge shift increases from 22 to 23 to 24 in going from fluorine to chlorine to bromine.

All dipole moments of complexes were computed assuming no dissociation of the complex. The resulting errors in the moments of the complexes were estimated where dissociation constants were available. In all cases studied here k'_c, where known, was 2×10^{-4} or less and the resulting error in the moment of the complex was too small to be significant.

The observed and calculated dipole moments of some substituted pyridine compounds are listed in Table 18.

TABLE 18

OBSERVED AND CALCULATED DIPOLE MOMENTS OF SOME SUBSTITUTED PYRIDINES

Compound	Observed	Calculated[1]
2-Fluoropyridine	3.39	3.15
3-Fluoropyridine	2.04	1.93
3-Chloropyridine	1.90	1.94
2,6-Dimethylpyridine	1.81	1.80

The agreement between observed and calculated dipole moments is fairly good.

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[1] Calculated from bond moments listed in Smyth (58).

SUMMARY

A series of new molecular complexes has been prepared. Complexes of iodine pentafluoride with pyridine, 2-methylpyridine, dioxane, 2-fluoropyridine, and trifluoroacetic anhydride have been made. Complexes of IBr, ICl and ICl_3 with dioxane and a variety of substituted pyridine derivatives have been made. Melting points, molecular formulae and qualitative observations of the colors and stabilities of most of the complexes have been tabulated.

The electric moments of 3-chloropyridine, 2-fluoropyridine, 3-fluoropyridine and 2,6-dimethylpyridine have been measured in benzene solution at 25° C. The electric moments of seventeen molecular complexes of organic amines and ethers with interhalogen compounds have been measured at 25° C. in solution in a nonpolar solvent. The results were interpreted in terms of a model in which a lone pair of electrons of the nitrogen or oxygen atom is donated to the iodine atom of the interhalogen compound. The dative bond so formed is polar in character and the percent charge transfer was calculated for each complex from the difference between the observed moment and the moment calculated for no interaction. The dative bond was assumed to be linear with the axis of the interhalogen compound and the plane of the pyridine ring except in the case of iodine pentafluoride where

it was assumed to be at an angle of 30° to the axis of the tetragonal pyramidal molecule.

Partial phase diagrams were completed for the systems pyridine-iodine pentafluoride and dioxane-iodine pentafluoride. There is evidence of 1:1 compound formation in both systems and, in addition, of a 1:2 compound in the dioxane-iodine pentafluoride system. From the ultra violet absorption spectra of a series of solutions of the complexes in carbon tetrachloride the dissociation constants of five of the complexes were obtained.

APPENDIX A

A molecular complex of mercuric iodide with pyridine ($HgI_2 \cdot 2C_5H_5N$) was prepared. This white crystalline complex had a melting point of 100-101° C. The dipole moment was measured in benzene solution.

Zapolskii (70) found, from freezing point data in benzene, that the molecular weight was half of the expected value. The complex probably dissociates into pyridine and a monopyridine-mercuric iodide complex. On this assumption the total polarization of the monopyridine complex (P_3) was calculated from the equation

$$P_T = P_1 f_1 + P_2 f_2 + P_3 f_3 \qquad (28)$$

which is an extension of Equation 10 for a three component system. The total polarization P_T was calculated from

$$P_T = \frac{\mathcal{E}_{12} - 1}{\mathcal{E}_{12} + 2} \cdot \frac{M_1 f_1 + M_2 f_2 + M_3 f_3}{d_{12}} \qquad (29)$$

which is an extension of Equation 11.

The dipole moment found by use of these equations was 5.88 D. The value of the molar refraction of the monopyridine complex employed (66.2 cc.) was obtained by adding the molar refraction of pyridine and mercuric iodide.

The experimentally determined dielectric constants and specific volumes of the solutions are listed in Table 19.

TABLE 19

DIELECTRIC CONSTANTS AND SPECIFIC VOLUMES OF THE CARBON TETRACHLORIDE SOLUTIONS AT 25° C.

f_2	12	v_{12}
	Mercuric-Iodide Pyridine Complex	
0.00053	2.2530	0.6309
.00111	2.2858	.6307
.00199	2.3311	.6301
.00390	2.4447	.6279

APPENDIX B

The freezing points and cooling curves of some fluorocarbon derivatives were determined in connection with the cryoscopic work. The compounds were obtained from R. D. Dresdner of the University of Florida. The compounds and observed freezing points are listed in Table 20.

TABLE 20

FREEZING POINTS OF SOME FLUOROCARBON DERIVATIVES

Compound	Freezing Point
$(CF_3)_2NCOOCH_3$	-64.2° C.
$(CH_3)_2NOCCF_3$	-62.3° C.
$(C_2F_5)_2SF_4$	-87.0° C.
$C_4F_9SF_6$	-119.0° C.
$(C_2F_5)_3N$	Thickens to a glass -135 to -150° C.

BIBLIOGRAPHY

1. L. J. Andrews, Chem. Reviews, 54, 713 (1954).

2. H. S. Booth and W. C. Morris, Inorganic Synthesis, p. 167 Vol. 1, McGraw-Hill Book Co., Inc., New York, 1939.

3. E. A. Braude and F. C. Nachod, Determination of Organic Structures by Physical Methods, Chap. IV, Academic Press Inc., New York, 1955.

4. R. E. Buckles and J. F. Mills, J. Am. Chem. Soc., 75, 552 (1953).

5. J. A. Cathcart and D. D. Reynolds, J. Am. Chem. Soc., 73, 3504 (1951).

6. M. Chatlet, Compt. rend., 196, 1421 (1933).

7. M. Chatlet, Compt. rend., 196, 1607 (1933).

8. J. Chien, J. Chem. Educ., 24, 494 (1947).

9. J. Cornog and R. A. Karges, Inorganic Synthesis, p. 165 Vol. 1, McGraw-Hill Book Co., Inc., New York, 1939.

10. W. J. Curran and H. H. Wenzke, J. Am. Chem. Soc., 57, 2162 (1935).

11. B. C. Curran, J. Am. Chem. Soc., 63, 1470 (1941)

12. P. Debye, Polar Molecules, The Chemical Catalog Co., New York, 1929.

13. P. Debye, Physikal Z., 13, 97, (1912).

13a. F. Fairbrother, Nature, 160, 87 (1947); J. Chem. Soc. (1948) 1051.

14. Ya. A. Fialkov and I. D. Muzyka, J. Gen. Chem. (U.S.S.R.), 18, 1205 (1948), Chem. Abstracts 43,6901 (1949).

15. A. Findlay, The Phase Rule and Its Applications, Ninth Ed., Dover Publications, Inc., New York, 1951.

16. S. Glasstone, Textbook of Physical Chemistry, D. Van Nostrand Co., Inc., New York, 1946.

17. I. F. Halverstadt and W. D. Kumler, J. Am. Chem. Soc., 64, 2988 (1942).

18. K. Hartely and H. A Skinner, Trans. Faraday Soc., 46, 621 (1950).

19. O. Hassel, Molecular Physics, 1, 241 (1958).

20. O. Hassel and J. Hvoslef, Acta. Chem. Scand., 8, 873 (1954).

21. O. Hassel and J. Hvoslef, Acta. Chem. Scand., 10, 138 (1956).

22. O. Hassel and G. Eia, Acta. Chem. Scand., 10, 139 (1956).

23. G. Hedestand, Z. physik. Chem., B2, 428 (1929).

24. W. Hieber and E. E. Feder, Z. Electrochem., 44, 881 (1938).

25. International Critical Tables, Vol. 1, p. 58., McGraw-Hill Book Co., Inc., New York, 1926.

26. K. A. Jensen, Z. anorg. allgem. Chem., 250, 257 (1943).

27. R. M. Keefer and L. J. Andrews, J. Am. Chem. Soc., 77, 2164 (1955).

28. R. M. Keefer and L. J. Andrews, J. Am. Chem. Soc., 75, 3561 (1953).

29. J. A. A. Ketelaar, C. van de Stolpe, A. Goudsmit and W. Dzcubas, Rec. trav. chim., 71, 1104 (1952).

30. G. Kortüm and H. Walz., Z. Elektrochem., 57, 73 (1953).

31. R. J. W. Lefevre, Dipole Moments, p. 53, Methuen and Co., London, 1948.

32. L. S. Lilich and O. E. Presnikova, Uchenye Zapiski, Leningrad Gosudarst. Univ. im. A. A. Zhdanova, No. 163, Ser. Khim Nauk., No. 12, 3 (1953);Chem. Abstracts 49, 5939 (1955).

33. E. T. McBee, O. R. Pierce and D. D. Meyer, J. Am. Chem. Soc., 77, 83 (1955).

34. R. Müller, H. Kumpfmiller, and H. Baur, Z. anorg. allgem. Chem., 156, 65 (1926).

35. R. S. Mulliken, J. Am. Chem. Soc., 72, 600 (1950).

36. Mulliken and Reed, J. Am. Chem. Soc., 74, 3869 (1954).

37. W. B. Person, R. E. Humphery, W. A. Deskin and A. I. Popov, J. Am. Chem. Soc., 80, 2049 (1958).

38. P. Pfeiffer, Organische Molekülverbindugen, 2nd Ed., Ferdinand Enke, Stuttgart, Germany, 1927.

39. A. I. Popov and R. T. Pflaum, J. Am. Chem. Soc., 79, 570 (1957).

40. A. I. Popov and R. H. Rygg, J. Am. Chem. Soc., 79, 4622 (1957).

41. A. I. Popov and N. E. Skelly, J. Am. Chem. Soc., 76, 5309 (1954).

42. A. I. Popov and N. E. Skelly, J. Am. Chem. Soc., 77, 3722 (1955).

43. C. F. Prutton and S. H. Maron, Fundamental Principles of Physical Chemistry, the MacMillan Co., New York, 1951.

44. H. Rheinboldt and R. Boy, J. prakt. Chem., 129, 273-7 (1931).

45. H. Rheinboldt and R. Boy, J. prakt. Chem., 129, 268 (1931).

46. H. Rheinboldt, A. Luyken, and H. Schmittmann, J. prakt. Chem., 148, 81 (1937).

47. H. Rheinboldt, A. Luyken and H. Schmittmann, J. prakt. Chem., 149, 30 (1937).

48. G. R. Robertson, Ind. Eng. Chem. Anal. Ed., 11, 464 (1939).

50. A. Roe and G. F. Hawkins, J. Am. Chem. Soc., 69, 2443 (1947).

51. A. F. Scott and J. F. Bunnett, J. Am. Chem. Soc., 64, 2727 (1942).

52. R. L. Scott and T. M. Cromwell, J. Am. Chem. Soc., 72, 3825 (1950).

53. I. A. Sheka and K. F. Karlysheva, Zhur. Obshchei Khim, 21, 833 (1951), Chem. Abstracts 46-511 (1952).

54. I. A. Sheka, Zhur. Fiz. Khim, 109 (1956), Chem. Abstracts 50-9927 (1956).

55. I. A. Sheka, J. Phys. Chem., (U.S.S.R.), 16, 99 (1942), Chem. Abstracts 37- 6538 (1943).

56. I. A. Sheka, Zapiski Inst. Khim Akad. Nauk., (U.S.S.R.), 7, No. 1, 57 (1940), Chem. Abstracts 35-2379 (1941).

57. I. A. Sheka, Zhur. Obshchei Khim, 26, 26 (1956), Chem. Abstracts 50- 11748 (1956), English Trans. 50-15152, (1956).

58. C. P. Smyth, Dielectric Behavior and Structure, McGraw-Hill Book Co., Inc., New York, 1955.

59. Ya. K. Syrkin and K. M. Anisimova, Doklady Akad. Nauk, (U.S.S.R.), 59, 1457 (1948), Chem. Abstracts 42, 6593 (1948).

60. Ya. K. Syrkin and M. E. Dyatkina, Structure of Molecules and the Chemical Bond, Interscience Publishers Inc., New York, 1950.

61. H. Bradford Thompson, An Investigation of Certain Physical Properties of the Halogen Fluorides, doctoral thesis, Michigan State College (1953) p. 33.

62. H. Ulich, E. Hertel and W. Nespital, Z. physik. Chem., B17, 21 (1932).

63. H. Ulich and W. Nespital, Z. angew. Chem., 44, 750 (1931).

64. A. I. Vogel, J. Chem. Soc., 1833 (1948).

65. A. J. Werth, Jr., M. E. Hobbs and P. G. Gross, J. Am. Chem. Soc., 70, 800 (1948).

66. G. W. Wheland, The Theory of Resonance, John Wiley and Sons, Inc., New York, 1944.

67. D. M. Williams, J. Chem. Soc., 1931, 2783.

68. L. F. Yntema and V. Heimes, Trans. Kentucky Acad. Sci., 7, 85 (1938).

69. L. F. Yntema and R. Juhasz, J. Am. Chem. Soc., 62, 3522 (1940).

70. V. V. Zapolskii, State Inst. Tobacco Investigations, (U.S.S.R.), Bull. No. 81, 113 (1931), Chem. Abstracts 26, 6066, 26, 5024 (932).