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CHARGE-TRANSFER INTERACTIONS OF IODINE WITH A SERIES OF THIONES

by

Arthur Frederick Grand

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Doctoral Committee:

Professor Milton Tamres, Chairman
Professor Philip J. Elving
Assistant Professor Julien Gendell
Professor John R. Platt
Assistant Professor Paul G. Rasmussen

Abstract

CHARGE-TRANSFER INTERACTIONS OF IODINE
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The major portion of this work involved a spectrophotometric investigation in CCl_4 of the 1:1 iodine complexes with a series of thione donors containing the N-C=S group. The series included tetraethylthiuram disulfide (TETD), $(C_2H_5)_2N$-C(S)-SS-C(S)-$N(C_2H_5)_2$; tetramethylthiuram disulfide (TMTD), $(CH_3)_2N$-C(S)-SS-C(S)-$N(CH_3)_2$; tetramethylthiuram monosulfide (TMTM), $(CH_3)_2N$-C(S)-S-C(S)-$N(CH_3)_2$; methyl dimethyldithiocarbamate (MMDTC), $(CH_3)_2N$-C(S)-SCH_3; and N,N-dimethylthioacetamide (DMTA), $(CH_3)_2N$-C(S)-CH_3. The object of the study was to explore the predominance of a single electron donor site in these molecules which contain two or more possible donor sites.

Results for the study of the charge-transfer band in the ultraviolet region, and, in one case, for the blue-shifted iodine band in the visible region are summarized below. The enthalpy (kcal./mole) and the entropy (e.u.) of complex formation were determined from the temperature dependence of the stability constant (liters/mole) over the range 5-30°C. Error limits were calculated at the 90% confidence level.

TETD (UV): $K_{20°} = 182 \pm 34$; $-\Delta H^{\circ} = 6.38 \pm 0.80$; $-\Delta S^{\circ} = 11.4 \pm 2.7$

TETD(Vis): $K_{20°} = 281 \pm 9$; $-\Delta H^{\circ} = 6.62 \pm 1.11$; $-\Delta S^{\circ} = 11.3 \pm 3.8$

TMTD (UV): $K_{20°} = 152 \pm 19$; $-\Delta H^{\circ} = 7.18 \pm 0.62$; $-\Delta S^{\circ} = 14.4 \pm 2.1$

TMTM (UV): $K_{20°} = 433 \pm 148$; $-\Delta H^{\circ} = 7.30 \pm 0.66$; $-\Delta S^{\circ} = 13.0 \pm 2.3$

MMDTC(UV): $K_{20°} = 182 \pm 28$; $-\Delta H^{\circ} = 7.53 \pm 0.36$; $-\Delta S^{\circ} = 15.3 \pm 1.2$

DMTA (UV): $K_{20°} = 1990 \pm 90$; $-\Delta H^{\circ} = 9.77 \pm 0.37$; $-\Delta S^{\circ} = 18.3 \pm 1.3$

(The DMTA-I_2 complex showed two distinct absorption bands in the ultraviolet, one at 310 mμ, attributed to a charge-transfer transition, and the second at 340 mμ, attributed to a transition within the complexed donor.)

The relatively small effect of the substituents on the donor strengths of the molecules suggest that the same donor site is dominant in each case. Comparison of the data with those on related systems led to the conclusion that interaction with iodine occurs through the thiocarbonyl sulfur. For the iodine complex with dixanthogen, C_2H_5O-C(S)-SS-C(S)-OC_2H_5, which was investigated only briefly, there was a marked decrease in stability ($K_{20°} \simeq 5.3 \pm 0.7$ l./mole).

The investigation was extended to several metal ion complexes of the dithiocarbamates and, very briefly, of the xanthates. Here, the metal ion coordinates to the primary donor site of the ligand, leaving the secondary site available for possible donor-acceptor complex formation.

The interaction of iodine with the diethyldithiocarbamates, $(C_2H_5)_2NCS_2$, of mercury(II), lead(II), cadmium(II), and zinc(II) in chloroform cleaved the metal sulfur bonds to produce tetraethylthiuram disulfide (the dimer of the ligand)

and the metal iodide. This reaction was followed quantitatively by visual and spectrophotometric titration, which suggests its use as an analytical method for water-insoluble metal dithiocarbamates. A similar reaction was observed for the ethylxanthate, $C_2H_5OCS_2$, complexes of zinc(II) and cadmium(II).

Exploratory attempts were made to study the interaction of some electron acceptors (iodine, tetracyanoethylene, and tetracyanoquinodimethane) with coordinated ligands (8-hydroxyquinoline, N-nitroso-N-phenyl-hydroxylamine, pyridine-N-oxide, thiocyanate, thiosemicarbazide). These were unsuccessful, due largely to the fact that some of the species had very limited solubility in relatively "inert" solvents and due to their intense ultraviolet absorption bands.

To

my wife, Priscilla,

and to

my parents

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I would like to express my sincere appreciation to Professor Milton Tamres for his advice and willing assistance throughout this research, particularly in the preparation of the manuscript. It has been a rewarding experience to be closely associated with such a dedicated teacher. I also want to thank my wife for her patience throughout these busy times, and for her assistance in typing and in preparing the figures in this dissertation.

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INTRODUCTION

I. CHARGE-TRANSFER

The spectroscopic study by Benesi and Hildebrand (1) of iodine in organic solvents and the theoretical interpretation by Mulliken (2) provided the stimulus for further investigations of molecular "charge-transfer" complexes. The review book by Briegleb (3) is testimony to the fact that this field has attracted considerable interest since these publications.

A half-century of attempts by many workers to explain the reason for the different colors of iodine in various solvents (4, and references therein) preceeded the Benesi-Hildebrand study. Among the early workers were Hildebrand and Glascock (5) who, in 1909, showed by freezing-point depression measurements that iodine formed a 1:1 complex with certain solvents. Then, using simple colorimetry, they determined equilibrium constants for the formation of several iodine-solvent complexes and also obtained an enthalpy of reaction for one of them.

Nineteen years later, Getman (6) presented the first extensive spectroscopic study of iodine in various solvents. He found that the visible absorption maximum of iodine in so-called "violet" solvents, such as carbon tetrachloride,

hexane, benzene, and toluene, was between 520 and 540 mμ; and in "brown" solvents, such as alcohols, acetone, and pyridine, it was between 460 and 480 mμ.

In 1948, Kleinberg and Davidson presented a review of iodine solutions in organic solvents (4). The classification of iodine solutions into essentially two groups according to color was prevalent even then.

The study by Benesi and Hildebrand (1b) revealed that a very intense ultraviolet absorption appeared for solutions of iodine in benzene, toluene, xylene, and mesitylene, but not in n-heptane or carbon tetrachloride, in spite of very similar visible spectra in all of the solvents. This absorption was attributed to a "complex" since neither component alone absorbs in this region. They then developed an equation for determining the equilibrium constant of the reaction from spectroscopic data. This equation and others using the same basic concepts (7, 8, 9) are fundamental in the study of molecular complexes by spectrophotometric means.

Shortly after the Benesi and Hildebrand work appeared, Mulliken published a series of papers (10, 11, 2, 12, 13, 14) on the theoretical aspects of molecular complexes. He described the unique, intense ultraviolet absorption of the complex as an electron jumping from the donor to the acceptor, an "intermolecular charge-transfer." Molecular complexes that may be characterized by absorption spectroscopy have become generally known as "charge-

transfer complexes."

According to Mulliken (2), the ground state of the complex may be represented by

$$\Psi_N = a\,\Psi_o + b\,\Psi_1 + \ldots \qquad (1)$$

where Ψ_o represents the donor and acceptor before interaction (D---A) but including weak polarization forces, Ψ_1 represents the two species after an electron has been transferred from the donor to the acceptor (D^+---A^-), a and b represent the relative contribution of the two forms, and + ... represents any other possible modifications. The excited state of the complex is then

$$\Psi_E = a^*\,\Psi_1 - b^*\,\Psi_o + \ldots. \qquad (2)$$

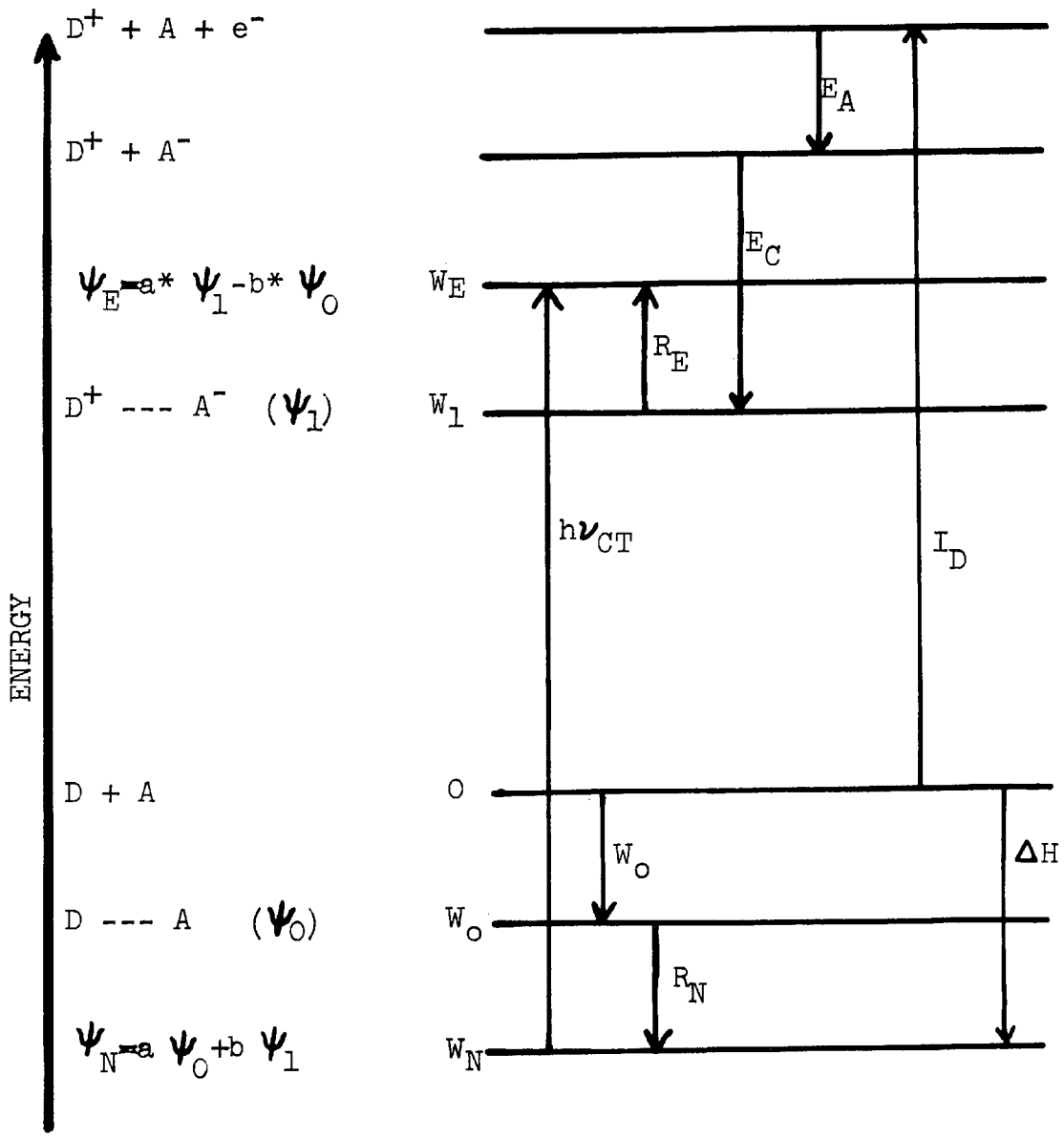
The charge-transfer excitation corresponds to the transition $\Psi_N \longrightarrow \Psi_E$.

Figure 1 illustrates the energy relationships involved in the formation of a complex between an electron donor and acceptor. The zero energy level is the energy of the two species at infinite separation. R_N and R_E are the small resonance energies that result from the interaction of Ψ_o and Ψ_1 to give Ψ_N and Ψ_E . The ionization potential of the donor, I_D, the electron affinity of the acceptor, E_A, and the coulombic interaction, E_C, of the ions D^+ and A^- are all shown.

From Figure 1,

$$W_N = -(W_o + R_N) = -\Delta H, \qquad (3)$$

Fig. 1. Energy level diagram for interaction of electron donor (D) and acceptor (A) (3, p. 3)



and

$$W_E = I_D - E_A - E_C + R_E = W_1 + R_E \; ; \qquad (4)$$

therefore,

$$h\nu_{CT} = -\Delta H + I_D - E_A - E_C + R_E \; . \qquad (5)$$

This fundamental relationship has been discussed in detail by Briegleb (3) and by Mulliken and Person (15).

The intramolecular transitions often are affected by complex formation. A "blue-shift" of the visible iodine band has been reported by many workers (e.g., 16, 17, 18, 19) and its origin has been discussed (13, 20). Lang has reported a blue shift of a donor absorption (17) and has discussed the correlation between extent of shift and strength of interaction.

There have been numerous reviews on various aspects of molecular complexes (3, 21, 15, 22, 23, 24). The most comprehensive review to date is Briegleb's book (3), published in 1961. However, the compilation of data in the book reflects the early predominant interest in aromatic π-electron donors, whereas the research presented in this thesis is primarily concerned with n-electron donors. Interest in charge-transfer studies of such molecules containing nitrogen, sulfur, and oxygen is more recent.

Iodine interactions with nitrogen-containing compounds were found to be extremely strong. For example, the iodine-triethylamine complex (25) was found to have

an enthalpy of reaction, ΔH, of about -12 kcal./mole, one of the strongest complexes reported. Even under the delocalizing influence of a π-electron system, the nitrogen-iodine interaction was strong (e.g., iodine-pyridine (26), with ΔH about -8 kcal./mole) compared to iodine complexes with aromatics (3, ΔH about -1 to -3 kcal./mole) or with ethers (27, ΔH about -4 to -6 kcal./mole). Iodine-diethyl sulfide interactions (28, 29, 30) were also found to be quite strong ($\Delta H \approx$ -8 kcal./mole), while the corresponding iodine-disulfide interactions (28, 29) somewhat weaker ($\Delta H \approx$ -5 to -7 kcal./mole).

In 1960 Drago and his co-workers began a series of studies (31, 32, 33, 34, 35, 16) on iodine complexes with amides and ureas. One of these (31) involves an infrared investigation of the iodine-dimethylacetamide (DMA) interaction. From the quantitative study of the decrease and shift of the carbonyl stretching frequency as a function of iodine concentration, the conclusion was reached that iodine interacts with oxygen rather than the nitrogen in this amide. His other studies using visible spectroscopy support this view.

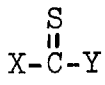
Studies have been reported on iodine charge-transfer complexes with thioamides, thioureas, and related donors (16, 17, 18, 36). These studies will be considered in detail in a later section.

Several X-ray studies of n-donor-halogen charge-transfer complexes have been made (e.g., 37, 38, 39, 40),

and showed in all cases that the donor atom and the two halogen atoms lie in a straight line. Similar structures have been assumed to exist in solution as well. However, solution studies have shown distinct 1:1 entities, while several of the X-ray analyses reveal a "chain" structure in the crystal with alternating donor and acceptor molecules (37, 39).

II. THE THIONES

The thiones are compounds having the structure XYC=S, where X and Y are groups which may contain nitrogen, sulfur or oxygen in addition to carbon and hydrogen. This class of compounds includes thioamides (I), thioureas (II), dithiocarbamates (III), thiuram disulfides (IV), thiuram monosulfides (V), xanthates (VI), and dixanthogens (VII).



(I) $X = NR_2$, $Y = R$

(II) $X,Y = NR_2$

(III) $X = NR_2$, $Y = SR$

(IV) $X = NR_2$, $Y = SS\text{-}C(S)\text{-}NR_2$

(V) $X = NR_2$, $Y = S\text{-}C(S)\text{-}NR_2$

(VI) $X = OR$, $Y = SR$

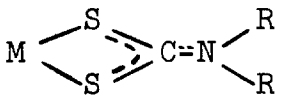
(VII) $X = OR$, $Y = SS\text{-}C(S)\text{-}OR$

$R = H$, alkyl, or aryl

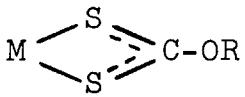
Electron delocalization among the n-donor atoms N,S, and O results in electronic and vibrational absorption spectra that are sometimes difficult to resolve, and has lead to controversy in the proper assignments of the absorption bands. This increases the difficulty in determining the proper donor site of these molecules.

One of the few areas in which there is relatively little disagreement among workers is in the structure of the thiones. Metal complexes of dithiocarbamates (41, 42,

43, 44, 45, 46) and xanthates (47) have been studied by X-ray techniques and the structures are represented by VIII and IX, respectively,

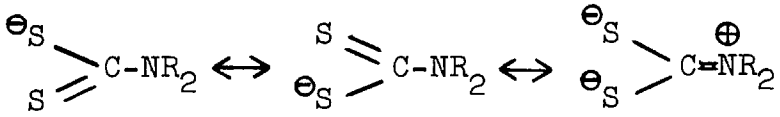


(VIII)



(IX)

(zinc diethyl- and dimethyldithiocarbamates have been found to be dimers in the crystalline state, but not in solution). The distances of the C-S and N-C bonds suggest considerable delocalization (as may be expressed by the three resonance structures X, XI, XII).



(X) (XI) (XII)

The corresponding resonance structure XII for nickel xanthate must contribute less since the C-O bond distance is normal. Both the xanthate and dithiocarbamate ligands are planar (except for the R groups).

The X-ray structure also has been reported (48) for tetraethylthiuram disulfide (structure IV, where R = C_2H_5), the dimer of the diethyldithiocarbamate ligand. The C-N bonds were again found to be shorter than normal, although not as short as in the metal complexes, indicating electron release by the nitrogen atoms. Each half of this molecule was found to be planar, with an angle of about 96° between planes. This angle is comparable to the dihedral angle of

dialkyl disulfides (49, 50, 51).

Truter's X-ray study (52) on thiourea (structure II, where R = H) showed C-N and C-S bond distances comparable to the dithiocarbamates, and it was concluded that strong conjugation effects were present. In a later study (53) on thioacetamide (structure I, where X = NH_2 and Y = CH_3), bond distances comparable to those of thiourea were reported, but it was suggested that the C-N linkage had no double-bond character and the C=S linkage was strictly a double bond. Planar structures in both cases, however, tend to favor some π-interaction.

Chatt, Duncanson, and Venanzi (54) were among the first to suggest that conjugation in the dithiocarbamate ligand caused the C-N stretching frequency of the metal complexes to appear at higher energies than expected. Slight shifts in this frequency were found among different metal ion complexes. Cotton and McCleverty (55) elaborated on this study, showing that the different inductive powers of methyl and ethyl groups on the dithiocarbamate ligand shifted the C-N frequency. Evtushenko (56) has investigated the C-S as well as the C-N frequency in several metal diethyldithiocarbamates.

There have been many differences of opinion among workers who have assigned an infrared frequency to C=S in compounds containing either the N-C=S group (57, 58, 59, 60, 61, 62, 63, 36) or the O-C=S group (59, 62, 64, 65, 66). Among the more recent papers is one by Jensen and Nielsen

(58) who present good arguments for locating the C=S frequency in thioamides and thioureas in the absorption region of a polar single bond rather than that of the normal double bond. They also suggest that the interaction of the N-C and C=S groups prevents exact assignment of any infrared bands to one of those linkages; however, certain frequencies may be assigned to an N-C=S grouping with a predominant contribution from either N-C or C=S.

The assignments of the electronic absorption bands of the thiones also are subject to some differences of interpretation. Janssen presented a comprehensive summary of ultraviolet and visible absorption data of thiones (67). He made assignments primarily on the basis of solvent band shifts and band intensities, and also on the effect of substituents (NR_2, SR, OR). He later (68) changed two of his assignments to bring them into agreement with $\pi \rightarrow \pi^*$ transition energies calculated by empirical LCAO-MO calculations. Other work by Shankaranarayana and Patel (69, 70) and Rao and co-workers (18, 71) based on similar techniques agree with Janssen's results.

In general, the lowest energy absorption appearing in most thiones has been assigned to an $n \rightarrow \pi^*$ transition ($\log \epsilon \leq 2$, where ϵ is molar extinction coefficient). The next highest energy absorption is usually assigned to a $\pi \rightarrow \pi^*$ transition. This is a very intense band ($\log \epsilon \sim 4$) and sometimes overshadows the weak $n \rightarrow \pi^*$ absorption. The next highest transition, of about the same intensity as

that for $\pi \rightarrow \pi^*$, is generally assigned as an $n \rightarrow \sigma^*$ transition. Solvent effects on the $\pi \rightarrow \pi^*$ and $n \rightarrow \sigma^*$ transitions are less pronounced than for the $n \rightarrow \pi^*$, which adds to making their assignments difficult.

The assignments of Hosoya, Tanaka, and Nagakura (72) for thioacetamide and thiourea are based primarily on molecular orbital calculations and polarized absorption spectra of crystals. They assigned the intense absorption band of lower energy to an "intramolecular charge-transfer" from the NH_2 group to the C=S group. Considering the strong conjugation in the N-C=S linkage, this assignment may not be inconsistent with the "$\pi \rightarrow \pi^*$" transition postulated by other workers. The intense band of higher energy was assigned to the localized $\pi \rightarrow \pi^*$ transition within the thiocarbonyl group.

Many of the thiones under discussion here have been studied as electron donors toward metal ions, hydrogen ions, iodine, and hydrogen-bonding acceptors. In discussing donor site toward any of these acceptors, it is important to remember that a strong donor toward one acceptor may not be a strong donor toward another acceptor (3, 73). Thus, a molecule with two possible donor sites may interact through different sites toward different acceptors, or both sites may interact with the same acceptor. Wayland and Gold (74) have shown that both alkyl thiocyanates (RSCN) and alkyl isothiocyanates (RNCS) interact with iodine and with phenol, which points out that either the

nitrogen or sulfur of the thiocyanate group (SCN) is capable of serving as a donor. Thiocyanate bridges are even possible (75), where the N and S atoms are linked to different acceptors.

There is little doubt that the dithiocarbamate ligand coordinates to metal ions through the sulfur atoms (see p. 9, discussion of X-ray studies). In the case of thiourea, coordination has been reported to occur through the sulfur or the nitrogen, depending on the metal ion (76), but most evidence points toward sulfur coordination (77, 78, 79).

Janssen, as well as others (80, 81, and references therein), supports the view that thioamides and thioureas are protonated on the sulfur. He refutes the arguments of Hosoya, Tanaka, and Nagakura (72) and of Spinner (82), who are strongly in favor of N-protonation. Janssen's arguments (80) are: (1) The $n \rightarrow \pi^*$ ultraviolet absorption either shifts considerably or disappears entirely in strong acid solution. (2) The ultraviolet spectrum of $(CH_3C(S)NH_2)H^+$ is similar to that of $CH_3C(NH)SCH_3$. (3) The infrared spectra of the hydrochloride salts of dimethylthioacetamide or tetramethylthiourea may be reasonably assigned to show S-H and C=N bonds and no N-H vibrations. (4) Nuclear magnetic resonance data of the protonated species show a significant barrier to rotation around the C-N bond, suggesting partial double-bond character.

Burrows and Hunter cite evidence (83) of intermolecular N-H---S=C hydrogen bonding in thio- and dithiocarbamate

esters. Truter's X-ray studies (53, 84) suggest N-H---S intermolecular bonding in thioacetamide and ethylenethiourea. Drago, et. al., reported a brief hydrogen bonding study with phenol and dimethylthioacetamide (16) in which he suggests that the thiocarbonyl sulfur is again the electron donor toward hydrogen.

Studies of the thiones as donors toward iodine (16, 17, 18, 36, 85) will be discussed later.

STATEMENT OF THE PROBLEM

Electron donor-acceptor interactions with substituted thiones containing two or more donor sites have been of much interest. Charge-transfer studies of iodine with thioamides (16, 17), thioureas (16, 17, 36), and related thiones (18) have been reported, and strong arguments have been presented for the thiocarbonyl sulfur being the predominant donor site. The present study was undertaken to further explore the predominance of a single donor site, and to see if related complex molecules also donate through that site alone.

A series of thione donors was selected whose structures are related by the presence of a "thioamide" group, N-C=S, but whose substituents are varied. The spectral and thermodynamic properties of the complexes formed between iodine and the members of the series should suggest whether or not the substituents have altered the donor site, or simply modified the donor behavior of the primary site.

The above problem was extended to ligands which coordinate with metal ions, and which contain two or more possible electron donor sites, such as the dithiocarbamates. If the predominant donor site of the ligand becomes coordinated to a metal ion, it may become possible for the secondary donor site to interact with another acceptor molecule. Studies of this nature were undertaken to determine the effects of a series of metal ions on the donor properties of the ligand.

PROCEDURE

I. CALCULATIONS

The study of charge-transfer complexes by spectrophotometric techniques is based on Beer's Law relating the concentration of an absorbing species to the amount of light absorbed by that species. This may be expressed by

$$A = \epsilon bC, \tag{6}$$

where A is the absorbance, ϵ is the extinction coefficient, b is the path length, and C is the concentration of the species. The units of b and C are usually cm. and moles/liter, respectively, and ϵ is then liters/mole-cm. If more than one species in the solution absorbs at the particular wavelength,

$$A_{total} = A_1 + A_2 + \ldots + A_n. \tag{7}$$

For the interaction of a donor, D, and iodine, I_2, to form a 1:1 complex, $D + I_2 \rightleftharpoons D{:}I_2$, the stability constant, K, in terms of concentrations may be written as

$$K = \frac{C}{(D_o - C)(I_o - C)}; \tag{8}$$

where C is the equilibrium concentration of complex, and D_o and I_o are the initial concentrations of donor and iodine, respectively. Taking the reciprocal of each side

in equation 8 gives

$$\frac{1}{K} = \frac{D_o I_o}{C} - D_o - I_o + C, \tag{9}$$

which is a quadratic equation in C. For weak complexes, C is small and, hence, the last term in equation 9 may be neglected. This gives

$$\frac{1}{K} = \frac{D_o I_o}{C} - D_o - I_o, \tag{10}$$

which is a linear equation in C. Further, if $D_o >> I_o$, then the term $-I_o$ may be neglected also and equation 11 results

$$\frac{1}{K} = \frac{D_o I_o}{C} - D_o \tag{11}$$

The effect of these approximations has been discussed by Tamres (86) and by Drago and Rose (87).

The spectrophotometric equivalents (substituting $C = A/\epsilon b$ from equation 6) of equations 9, 10, and 11 are equations 12, 13, and 14, respectively.

$$\frac{D_o I_o b}{A} = \frac{1}{\epsilon}(D_o + I_o) + \frac{1}{K\epsilon} - \frac{A}{b\epsilon^2} \tag{12}$$

$$\frac{D_o I_o b}{A} = \frac{1}{\epsilon}(D_o + I_o) + \frac{1}{K\epsilon} \tag{13}$$

$$\frac{D_o I_o b}{A} = \frac{D_o}{\epsilon} + \frac{1}{K\epsilon} \tag{14}$$

Equation 14 is the "Scott" equation (8), which is a rearrangement of the Benesi-Hildebrand equation (1b). Equation 13 will be referred to here as the "modified" Scott equation" or the "linear equation." Equation 12 will be referred to here as the "full equation." In this work, K and ϵ were calculated using both equations 12 and 13.

If the donor and acceptor also absorb in the same region as the complex, then the absorbance A, above, must be replaced by A', where

$$A' = A_{total} - A_{D_o} - A_{I_o} \qquad (15)$$

(A_{I_o} and A_{D_o} are the absorbances of the initial concentrations of iodine and donor). Then ϵ, above, becomes ϵ', where

$$\epsilon' = \epsilon_C - \epsilon_D - \epsilon_{I_2}. \qquad (16)$$

The extinction coefficient of the complex, ϵ_C, is then obtained from this relationship. It should be noted here that iodine does not obey Beer's Law at wavelengths below about 380 mμ, due probably to formation of I_4 (88,89). The extent to which I_4 might affect the results for the wavelengths and concentration ranges used in this study was investigated, and it was found that no significant error resulted.

Equation 13 is in the form of the equation for a straight line, $y = mx + b$. If, then, one plots D_oI_ob/A vs. $(D_o + I_o)$, ϵ can be determined from the slope $(1/\epsilon)$ and K can be determined from the slope/intercept ratio

$(K\epsilon/\epsilon)$. Equation 12 is quadratic in ϵ and was solved by a least-squares analysis (although an iterative procedure also can be employed). An IBM 7090 computer was used for all calculations.

The spectrophotometric equations 12, 13, and 14 are applicable to any wavelength where the absorbance is dependent on complex formation. Generally, the maximum of the "charge-transfer" band or that of the blue-shifted iodine band is selected. In the present study, in order to minimize the error, absorbance data taken at several wavelengths around the band maximum are all used to determine K and ϵ. The method involved is that proposed by Liptay (3, pp. 208-219). Calculations were made using the computer program written by Duerksen (90).

Briefly, the method is as follows. A matrix of absorbances, corrected for absorbance of donor and acceptor, is constructed for Q solutions (S) and P wavelengths (λ).

	S_1	S_2	-----	S_Q
λ_1	A_{11}	A_{12}	-----	A_{1Q}
λ_2	A_{21}	A_{22}	-----	A_{2Q}
.	.	.		.
.	.	.		.
.	.	.		.
.	.	.		.
λ_P	A_{P1}	A_{P2}	-----	A_{PQ}

(17)

A standard wavelength (usually the absorbance maximum), say λ_2, is selected, and each absorbance in each column is divided by the absorbance at λ_2.

	S_1	S_2	----	S_Q	Ave.
λ_1	A_{11}/A_{21}	A_{12}/A_{22}	----	A_{1Q}/A_{2Q}	$E_1 = \epsilon_1/\epsilon_2$
λ_2	1.00	1.00	----	1.00	$E_2 = 1.00$
	.	.		.	.
	.	.		.	.
	.	.		.	.
	.	.		.	.
λ_P	A_{P1}/A_{21}	A_{P2}/A_{22}	----	A_{PQ}/A_{2Q}	$E_P = \epsilon_P/\epsilon_2$

(18)

This normalizes each solution to λ_2, i.e., gives the ratio of ϵ at any wavelength to that at λ_2 for each solution. If the data are consistent, the values across each row should be equal to within reasonable error limits. The average of these results is given in the last column.

Each average E_i ($i = 1$ to P) is then divided into the absorbances for that wavelength in the original matrix. For solution Q at every wavelength λ_i, for example,

$$\frac{A_{iQ}}{E_i} = \frac{\epsilon_i bC_Q}{\epsilon_1/\epsilon_2} = \epsilon_2 bC_Q.$$

Thus, all the absorbances for each solution are normalized to λ_2 (third matrix, equation 19). The average of these normalized absorbances is the absorbance used in equations 12 and 13 to determine K and ϵ.

	S_1	S_2	----	S_Q
λ_1	A_{11}/E_1	A_{12}/E_1	----	A_{1Q}/E_1
λ_2	A_{21}/E_2	A_{22}/E_2	----	A_{2Q}/E_2
.	.	.		.
.	.	.		.
.	.	.		.
.	.	.		.
λ_P	A_{P1}/E_P	A_{P2}/E_P	----	A_{PQ}/E_P
Ave.	$\epsilon_2 b C_1$	$\epsilon_2 b C_2$	----	$\epsilon_2 b C_Q$

(19)

The Liptay procedure offers a means to check on the presence of more than one complex. If additional complexes are formed, then the values across each row in the second matrix (equation 18) should not be identical. Also, if the complexes have different ϵ's at different wavelengths, then this should show up in the third matrix (equation 19) as a deviation in the normalized absorbance as a function of wavelength.

From the temperature dependence of the equilibrium constant, the enthalpy and entropy of the interaction can be calculated from the relationship

$$-RT\ln K = \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ; \qquad (20)$$

where R is the gas constant, T is the absolute temperature, and ΔG°, ΔH°, and ΔS° are the standard free energy, enthalpy, and entropy changes, respectively, for a standard state of one molar solution. Equation 20 can be rearranged

to give

$$\log K = \frac{-\Delta H^{o}}{2.303RT}\frac{1}{} + \frac{\Delta S^{o}}{2.303R}, \qquad (21)$$

which is an equation of a straight line. From a plot of log K vs. $1/T$, ΔH^{o} can be obtained from the slope and ΔS^{o} from the intercept.

Since the equilibrium constant is calculated from the ratio $K\epsilon/\epsilon$, and ϵ is subject to error, the $K\epsilon$ product is found with greater precision than is K alone. Thus, unless ϵ_c varies systematically with temperature, it is preferable to average these ϵ's and to calculate the quotient $K\epsilon/\epsilon_{ave}$ (or K') at each temperature. It is K' that was used in equation 21 to calculate the thermodynamic data.

II. APPARATUS AND EXPERIMENTAL PROCEDURE

A Cary 14 double-beam, recording spectrophotometer was used for most of the spectral measurements. A Cary 11 and a Beckman DU also were used at times. The Cary 14 has a linear wavelength scan with a range of 185-3000 mμ, and has a linear absorbance scale with a range of 0-2.0. Most readings were taken from the recorded graph, but periodic static readings were made to check the absorbance scale of the chart with that of the recorder. These checks were satisfactory.

All measurements were made in the visible-ultraviolet region 600-200 mμ. A tungsten lamp was used as the light source for the region 600-400 mμ, and a hydrogen lamp for the region 400-200 mμ. A photomultiplier detector was used for all wavelengths.

The wavelength scan speed can be an important variable when readings are to be taken from the recorded graph. If the speed is too fast, the pen may not be able to respond quickly enough and the readings will be inaccurate. Too slow a speed only produces a graph much more expanded than is necessary. It was found that average scan speeds of 25 and 10 Å/sec. with a 5 inch/minute chart speed allowed better than 99% response by the pen. The slower speed produced a graph from which accurate readings at any single wavelength (in mμ) could be taken.

The slit width controls the resolution of the absorption bands. A very narrow slit would produce fine resolution, but the signal/noise ratio would be low and the readings would be inaccurate. A large slit would produce a high signal/noise ratio, but the resolution would be low. For this work, the slit was adjusted to produce resolution of better than 10 Å (1 mμ). This is adequate, considering the broad nature of many of the absorption bands studied. This resolution was calculated from the dispersion of the monochrometer as stated in the Cary manual.

The spectrophotometric cell was kept in a special cell housing (from Cary Instruments) in the Cary's sample compartment through which water was circulated from a constant temperature bath. The temperature control system is outlined schematically in Figure 2. A large water bath (A) contains a stirrer, a lamp, and cooling coils connected to an ice-water bath (containing its own pump). The temperature sensing and control mechanism (B) consists of a fixed-temperature mercury thermostat (H-B Instrument Company) and an accurate mercury thermometer. The thermostat is connected to a relay system (C) which controls the heating and cooling elements. The contacts on each thermostat are at fixed positions corresponding to temperatures between 5 and 30°C. When the temperature is low, there is no electrical contact and the relay maintains the lamp on and the ice-water bath off. When the temperature is high, the electrical contact keeps the lamp off and the ice-water

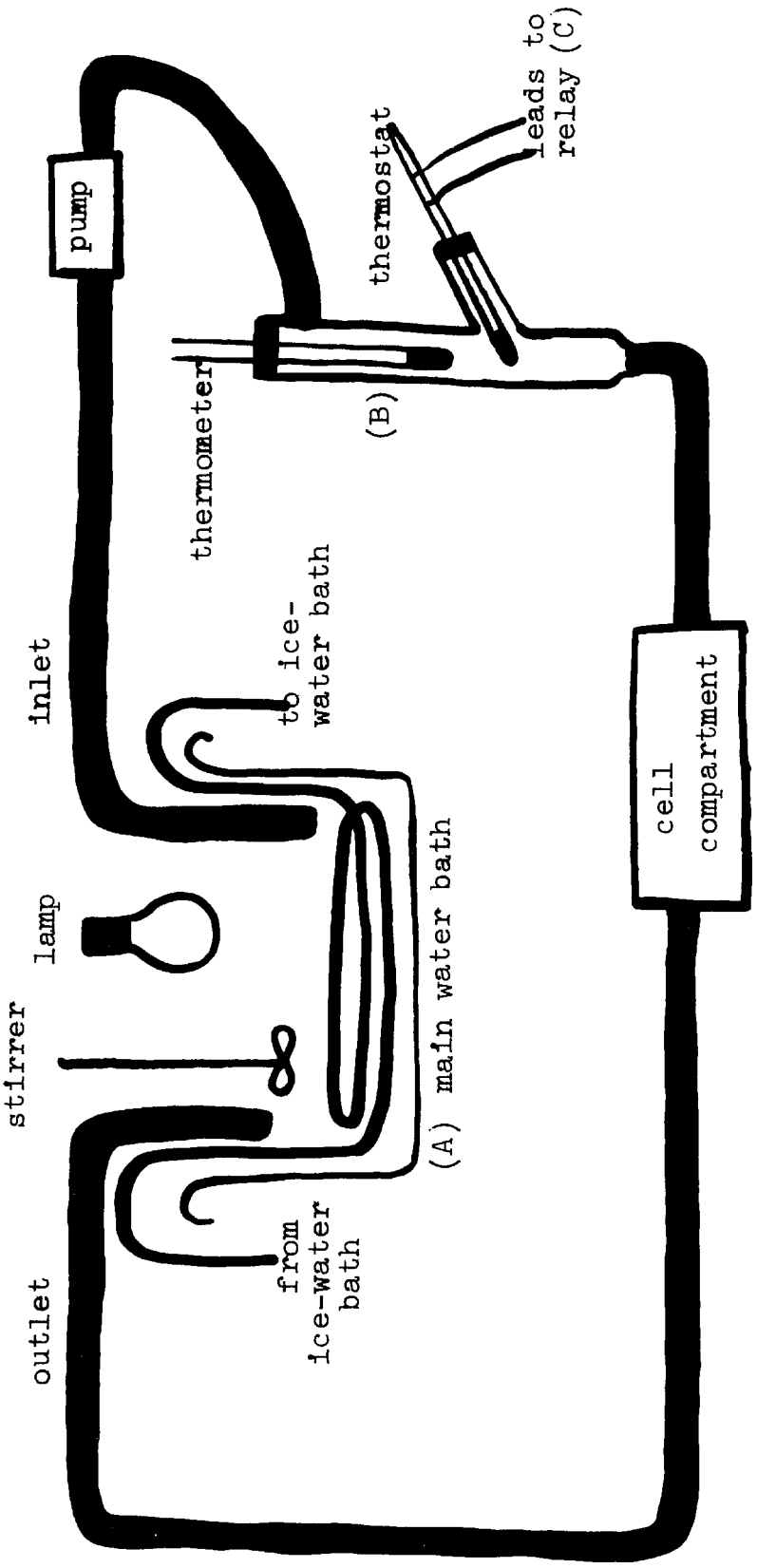


Fig. 2. Temperature control system

bath on. Temperature control was maintained to within $\pm$ 0.2°C.

Stock solutions of donor and of iodine were freshly prepared before each series of measurements by weighing the samples in glass-stoppered flasks on an analytical balance. Solvent was added and weighed, and the volume of solvent was determined from its density (91). Except for dixanthogen, the volume of solute was negligible. Stock solutions were diluted by volume at a constant room temperature (near 20°C). Concentrations were calculated for a "standard" temperature (usually 20.0°C); therefore, the concentration at any other temperature t was calculated from the density ratio of the pure solvent at t to that at the standard temperature. The concentration of stock solutions was checked spectrophotometrically.

Mixtures of desired donor and iodine concentrations were prepared by taking volume aliquots from the stock solutions. One cm. rectangular quartz cells with ground-glass stoppers were used for spectral measurements. A solution containing a donor-acceptor mixture was assumed to be at temperature equilibrium when the absorbance at the charge-transfer maximum stayed constant with time. Generally, 10-15 minutes was sufficient for a solution at room temperature to equilibrate to any temperature between 5 and 30°C.

The absorbance of each solution was usually measured at several temperatures during one run. A check on the

stability of the mixtures was made by returning to the initial temperature at the end of the run. Since the reference cell was not in a thermostated compartment, appropriate corrections had to be made for the temperature dependence of the solvent's absorption; however, this correction was negligible at the wavelengths and temperatures used for quantitative measurements.

RESULTS AND DISCUSSION

I. CHARGE-TRANSFER INTERACTIONS OF IODINE WITH FIVE THIONES

All complexes reported in this section had the following characteristics: (1) They were easily reversible. This was indicated by the reproducibility of absorbances at one temperature after changes in temperature. (2) They were of 1:1 composition. This was indicated by conformity of the data to an equation based on 1:1 complex formation (modified Scott equation), and by the lack of systematic deviations in the Liptay analysis. (3) Each complex exhibited a very intense ultraviolet absorption band, attributable to a "charge-transfer" transition.

For simplicity, the following terms and abbreviations will be used in this section:

D_o - initial concentration of donor

I_o - initial concentration of iodine (I_2)

A - absorbance

K_1 - equilibrium constant obtained from the linear or modified Scott equation (equation 13)

K_2 - equilibrium constant obtained from the full equation (equation 12)

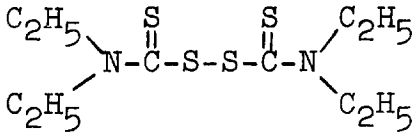
ϵ_c - molar extinction coefficient of the complex

ϵ_{ave} - average of ϵ_c's over all temperatures

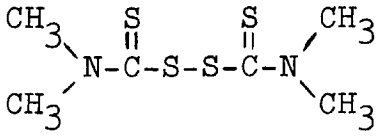
K' - a K based on the average value of ϵ, found by dividing $K_2\epsilon_c$ by ϵ_{ave}

All error limits were calculated at the 90% confidence level, except for ϵ_{ave} where the error limits are standard deviations.

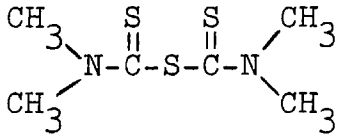
TETD - Tetraethylthiuram disulfide,



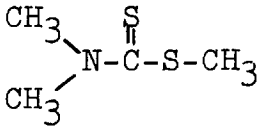
TMTD - Tetramethylthiuram disulfide,



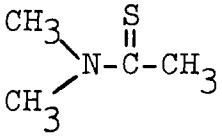
TMTM - Tetramethylthiuram monosulfide,



MMDTC - Methyl dimethyldithiocarbamate,



DMTA - N,N-dimethylthioacetamide,



A. TETD-I_2 (ultraviolet)

The TETD-I_2 complex has an absorption maximum at 356 mμ in CCl_4 (Figure 3). Mixtures containing 1.5-5.3 x 10^{-5}M TETD and 2.3-5.6 x 10^{-3}M I_2 were investigated at 10, 15, 20, 25, and 30°C. The data obtained from these investigations are presented in Table XVII* and the modified Scott plots for this system are shown in Figure 4. Figure 5 shows the log K' vs. 1/T plot.

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*All data tables are in the Appendix.

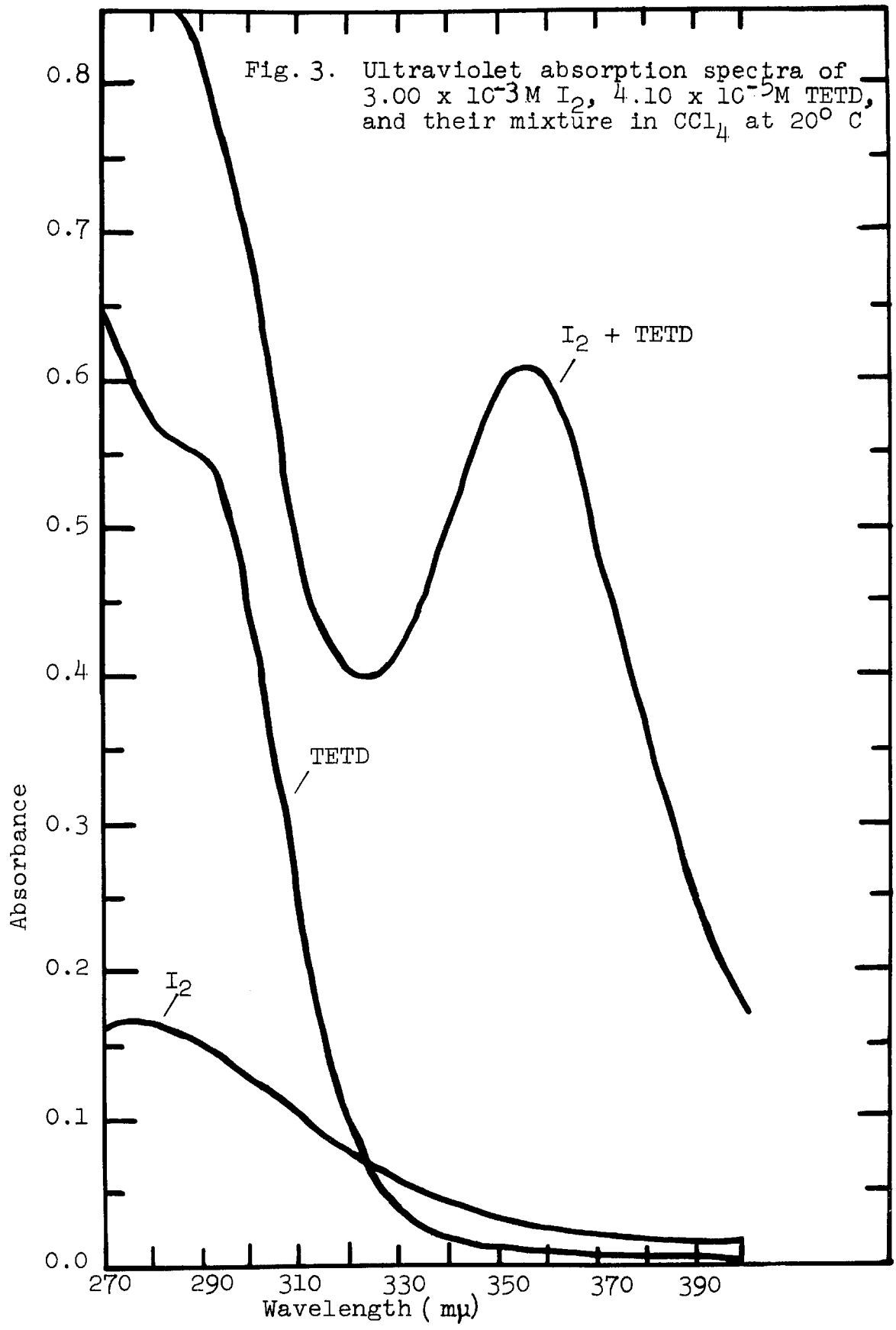


Fig. 3. Ultraviolet absorption spectra of 3.00×10^{-3} M I_2, 4.10×10^{-5} M TETD, and their mixture in CCl_4 at 20° C

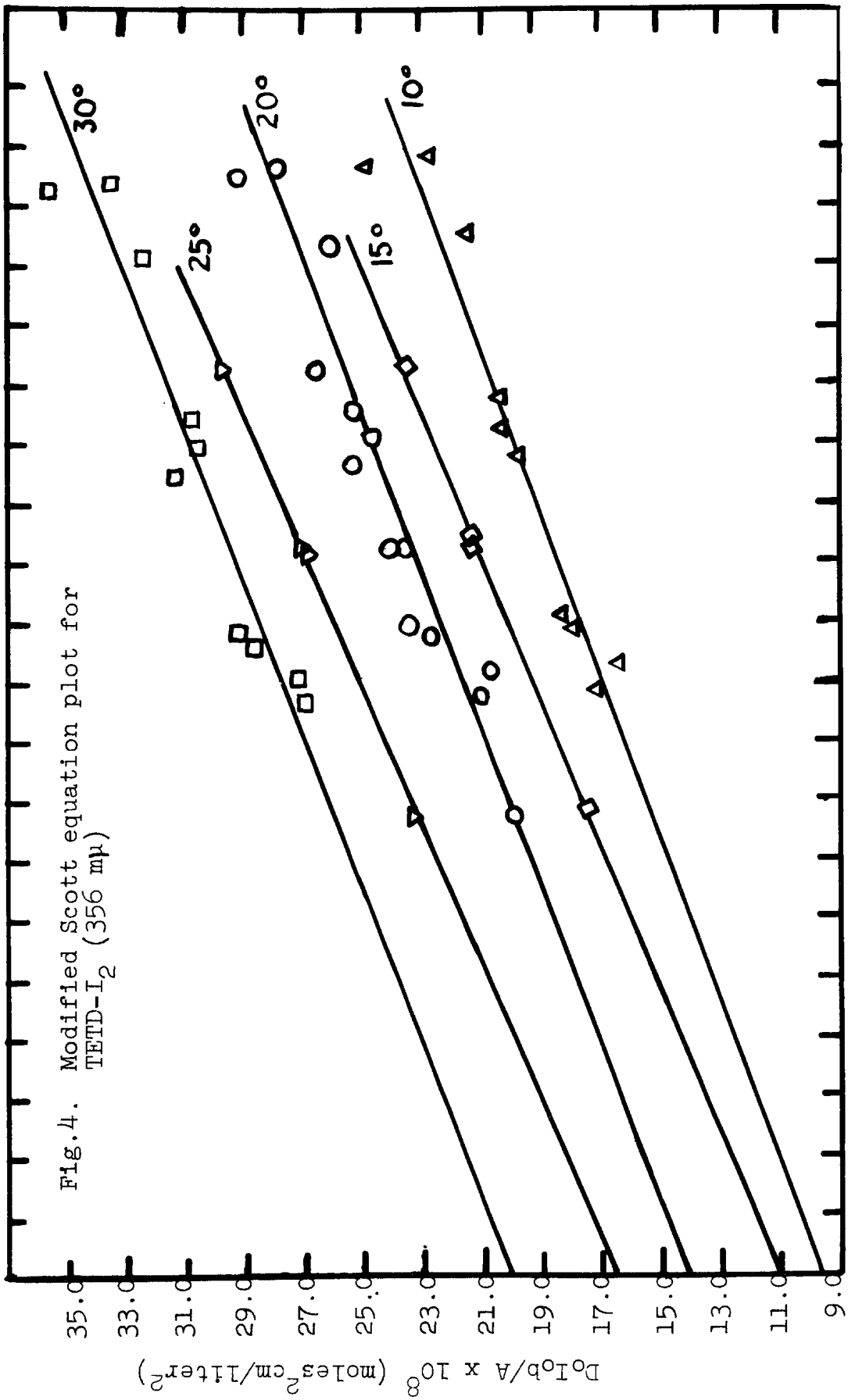


Fig.4. Modified Scott equation plot for TETD-I_2 (356 mμ)

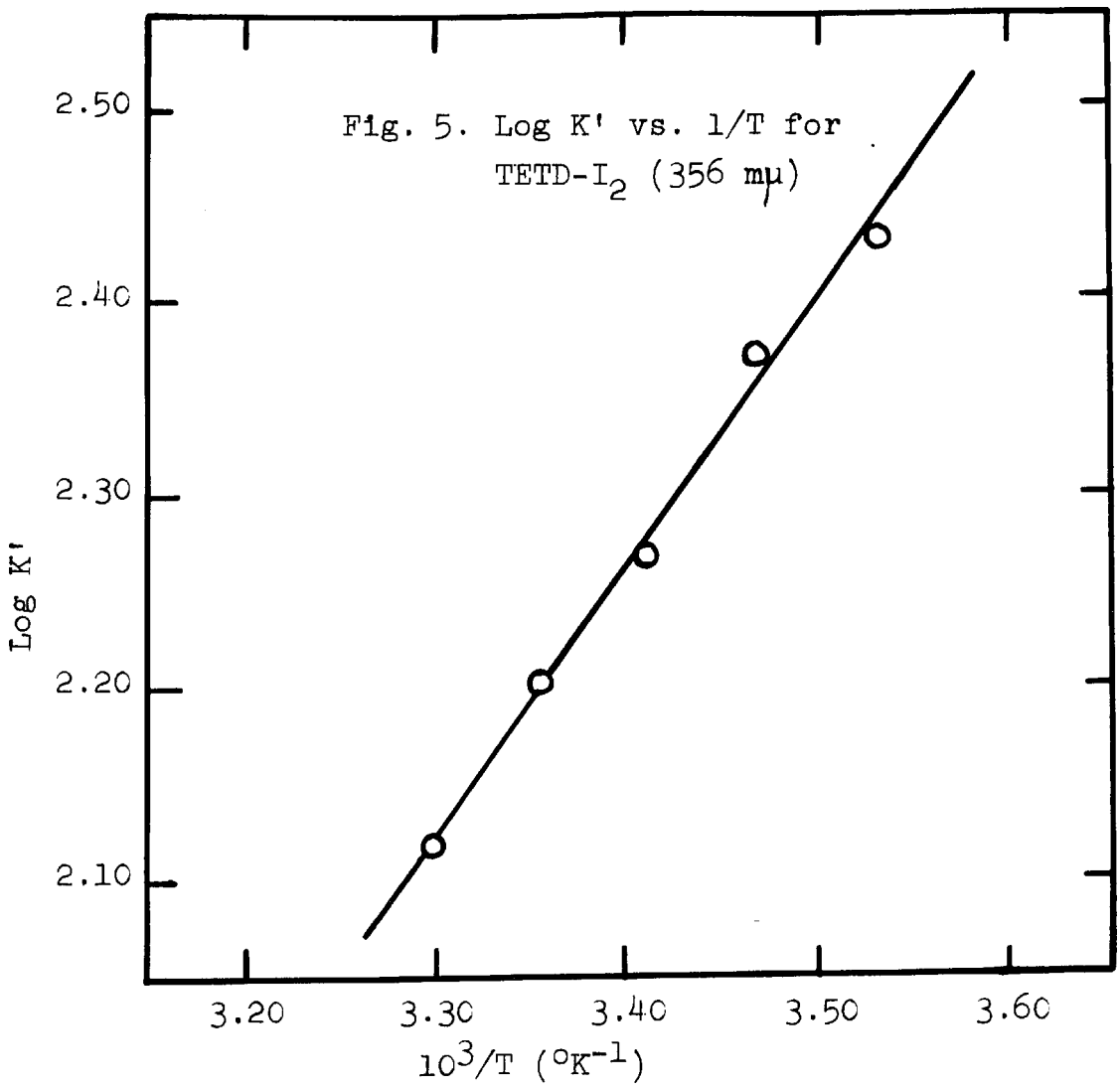


Fig. 5. Log K' vs. 1/T for TETD-I_2 (356 mμ)

TABLE I. Summary of results for TETD-I_2 (356 mμ)

K, ε obtained by Liptay analysis
Thermodynamic data based on values of K'

Temp.(°C)	K_1(liter/mole)	K_2(liter/mole)	ϵ_c(liter/mole-cm.)
30.0	128 ± 31	128	3.90×10^4
25.0	175 ± 21	175	3.47
20.0	182 ± 34	182	3.90
15.4	250 ± 21	250	3.63
10.0	254 ± 67	253	4.10

$\epsilon_{ave.} = (3.80 \pm .22)$

$\Delta H^o = -6.38 \pm 0.80$ kcal./mole

$\Delta S^o = -11.4 \pm 2.7$ e.u.

$\Delta G^o_{298} = -3.00$ kcal./mole

A summary of the results for the TETD-I_2 interaction is presented in Table I. No unusual experimental difficulties were encountered with this system and the data are considered to be reliable. This system showed more scatter than some of the others investigated, but more data points were taken to improve the statistical evaluation.

B. TETD-I_2 (visible)

Since TETD is colorless, and the TETD-I_2 complex appeared to be stable at relatively high concentrations, it was possible to make an independent study based on measurement of the blue-shifted visible iodine band. The shifted band has a maximum around 450-460 mμ which appears as a shoulder on the tail of the charge-transfer band (Figure 6). The uncomplexed iodine has a band maximum at 516 mμ. An isosbestic point, indicative of equilibrium between only two absorbing species, was located in the TETD-I_2 mixtures at 513 mμ.

Table XVIII gives the data for this study at 10, 20, and 30°C for 3.8×10^{-4} M I_2 and $0.7\text{-}7.2 \times 10^{-3}$M TETD. Figures 7 and 8 show the modified Scott plots and log K_2 vs. 1/T plot, respectively. The wavelength selected for the measurements was 460 mμ because the free iodine absorption has a negligible temperature dependence at this wavelength, and because it is near the shifted band maximum.

Results for the visible study of TETD-I_2 are summarized in Table II. The ΔH° values from the ultraviolet

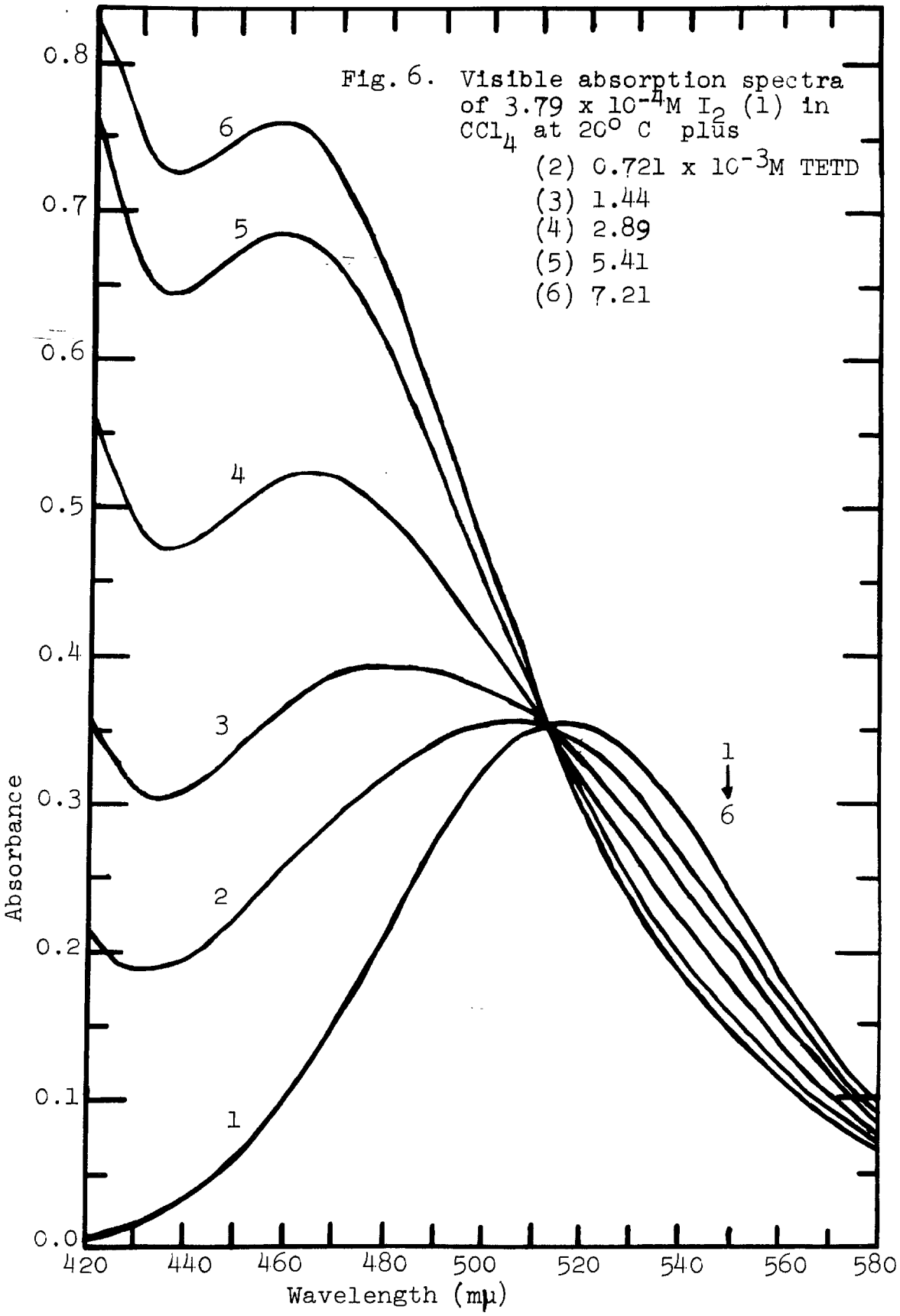


Fig. 6. Visible absorption spectra of 3.79 x 10^{-4}M I_2 (1) in CCl_4 at 20° C plus
(2) 0.721 x 10^{-3}M TETD
(3) 1.44
(4) 2.89
(5) 5.41
(6) 7.21

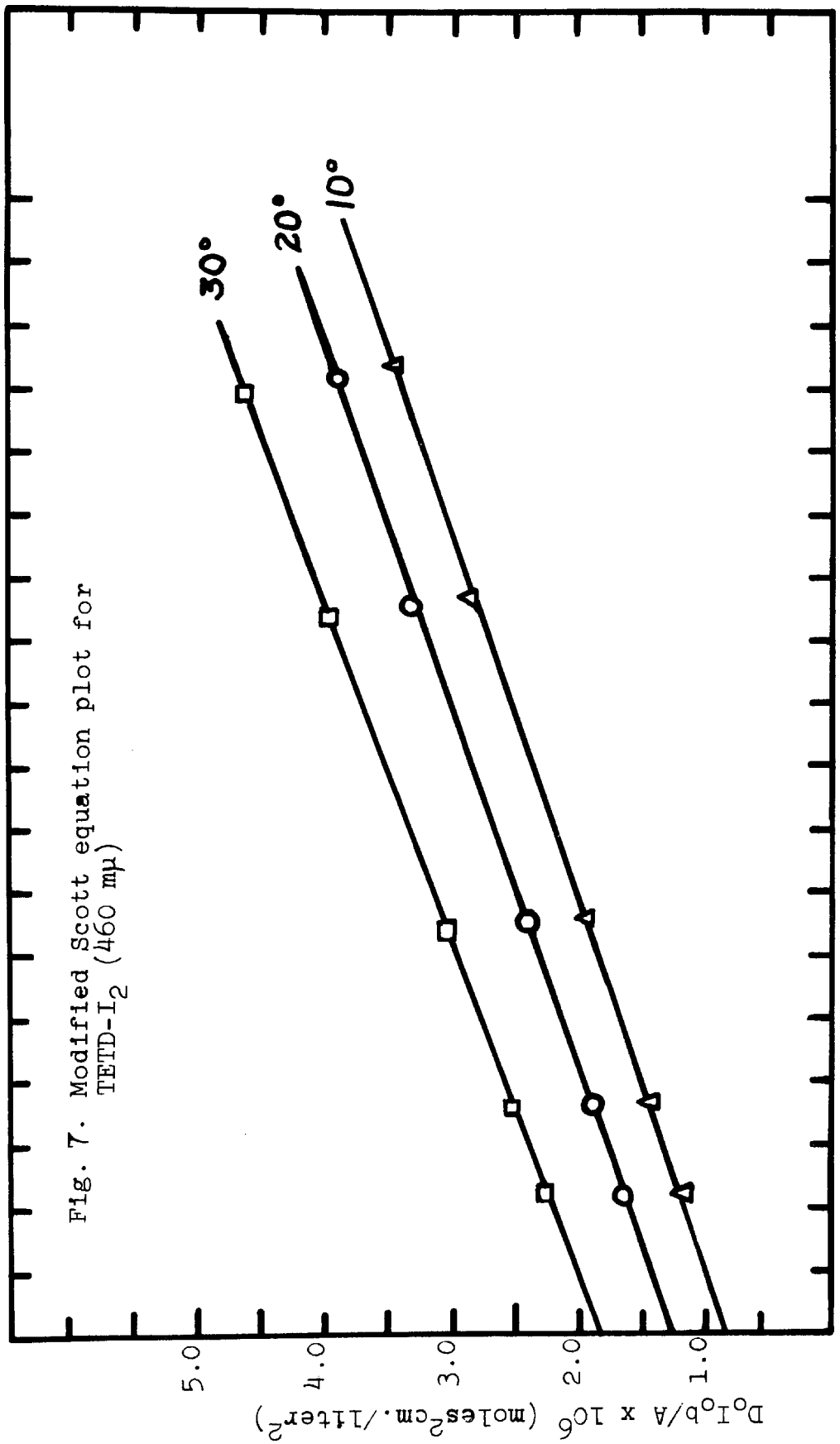


Fig. 7. Modified Scott equation plot for TETD-I_2 (460 mμ)

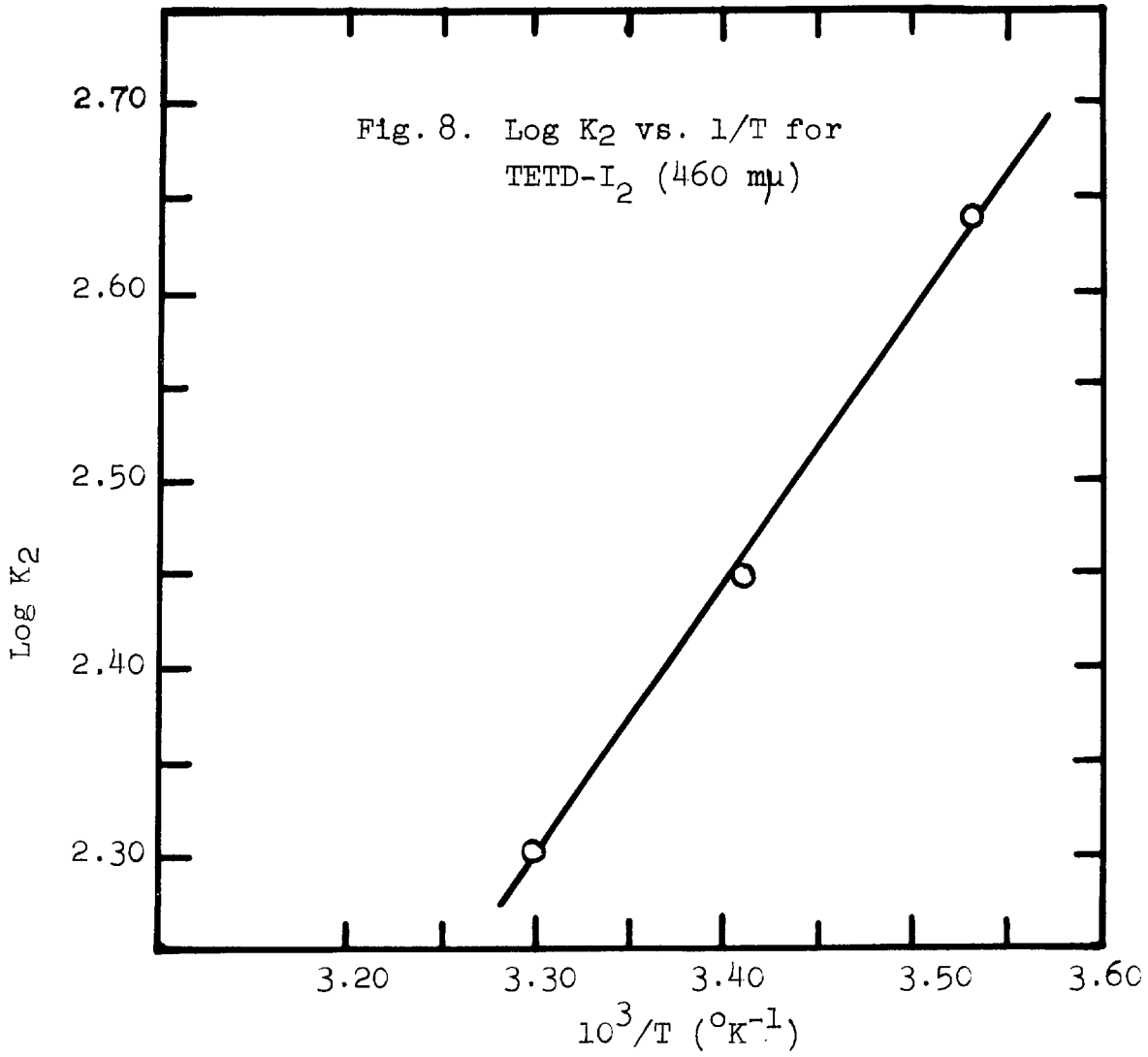


Fig. 8. Log K_2 vs. 1/T for TETD-I_2 (460 mμ)

TABLE II. Summary of results for TETD-I_2 (460 mμ)
K, ϵ obtained by Liptay analysis
Thermodynamic data based on the values of K_2

Temp. (°C)	K_1 (liter/mole)	K_2 (liter/mole)	ϵ_c (liter/mole-cm.)
30.0	197 ± 4	201	2.65 x 10^3
20.0	277 ± 9	281	2.77
10.0	439 ± 3	437	2.80

$\epsilon_{ave.} = (2.74 \pm .08)$

$\Delta H^o = -6.62 \pm 1.11$ kcal./mole

$\Delta S^o = -11.3 \pm 3.8$ e.u.

$\Delta G^o_{298} = -3.24$ kcal./mole

and visible studies are very close (-6.4 and -6.6 kcal./mole, respectively), although the equilibrium constants appear to be higher in the visible than in the ultraviolet study. The similarity in the results of these two independent studies suggests that a single complex is dominant over a large concentration range (0.4-5.6 x 10^{-3}M I_2 and 0.1-72.1 x10^{-4}M TETD).

C. TMTD-I_2

The TMTD-I_2 complex has an absorption maximum around 354 mμ in CCl_4 (Figure 9). Mixtures containing 4.7-
13.2 13.2 x 10^{-5}M TMTD and 1.3-3.8 x 10^{-3}M I_2 were investigated at 10, 15, 20, and 30°C. The data obtained from these studies are given in Table XIX and are plotted in Figure 10. The log K' vs. 1/T plot is shown in Figure 11.

Several of the solutions apparently underwent decomposition as evidenced by the changing absorbance reading on standing or the appearance of a precipitate. The data used in the calculations were reproducible and these solutions were shown to be stable.

The results for this system are summarized in Table III. The thermodynamic data were calculated using a log K' vs. 1/T plot, but the results of a log K_2 vs. 1/T analysis are included here for comparison. The difference in results between the two methods is small and indicates that the K and ε for these systems can be separated with a reasonable degree of accuracy. But it should be noted that the

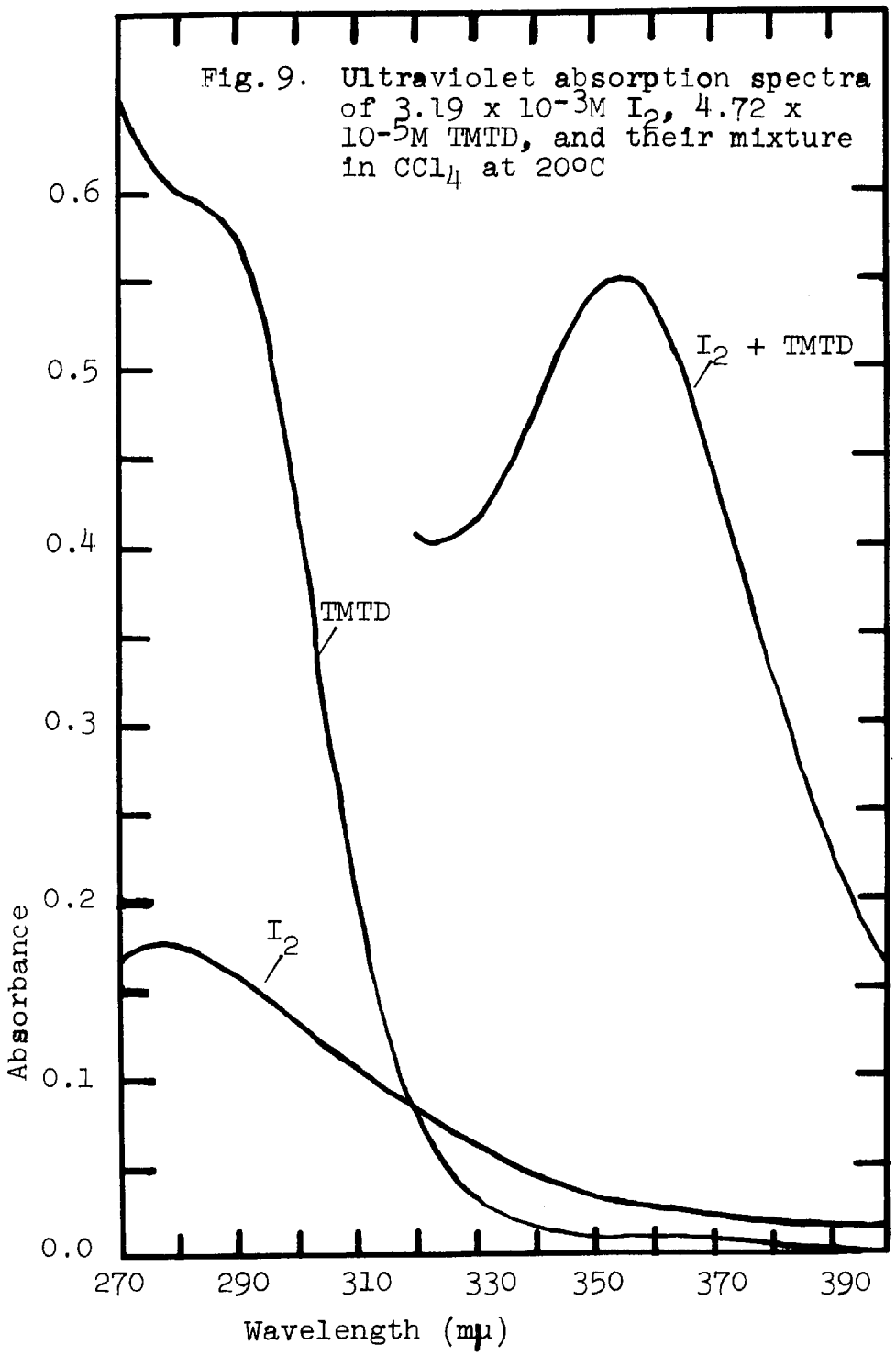


Fig. 9. Ultraviolet absorption spectra of 3.19×10^{-3}M I_2, 4.72×10^{-5}M TMTD, and their mixture in CCl_4 at 20°C

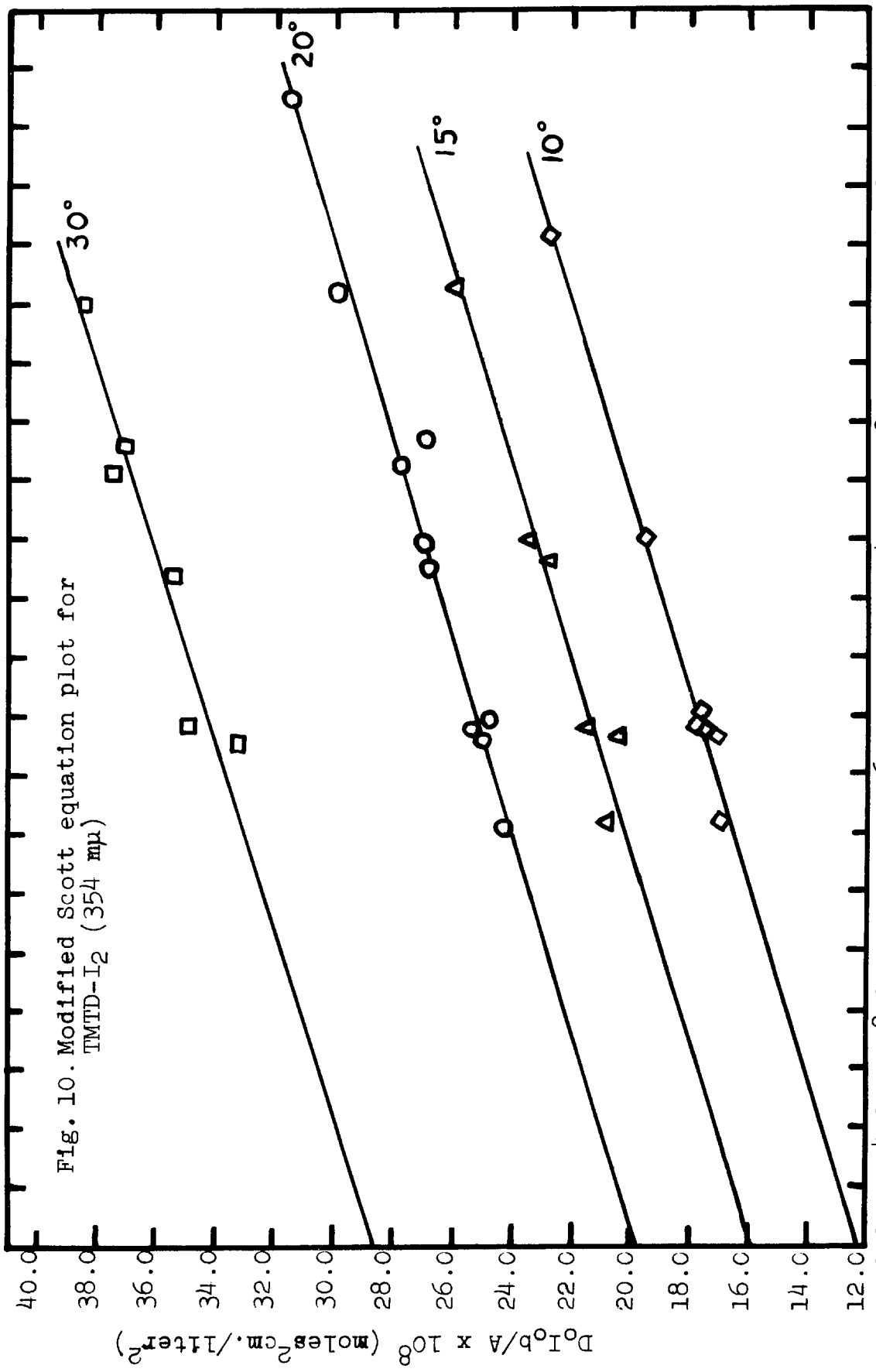


Fig. 10. Modified Scott equation plot for TMTD-I_2 (354 mμ)

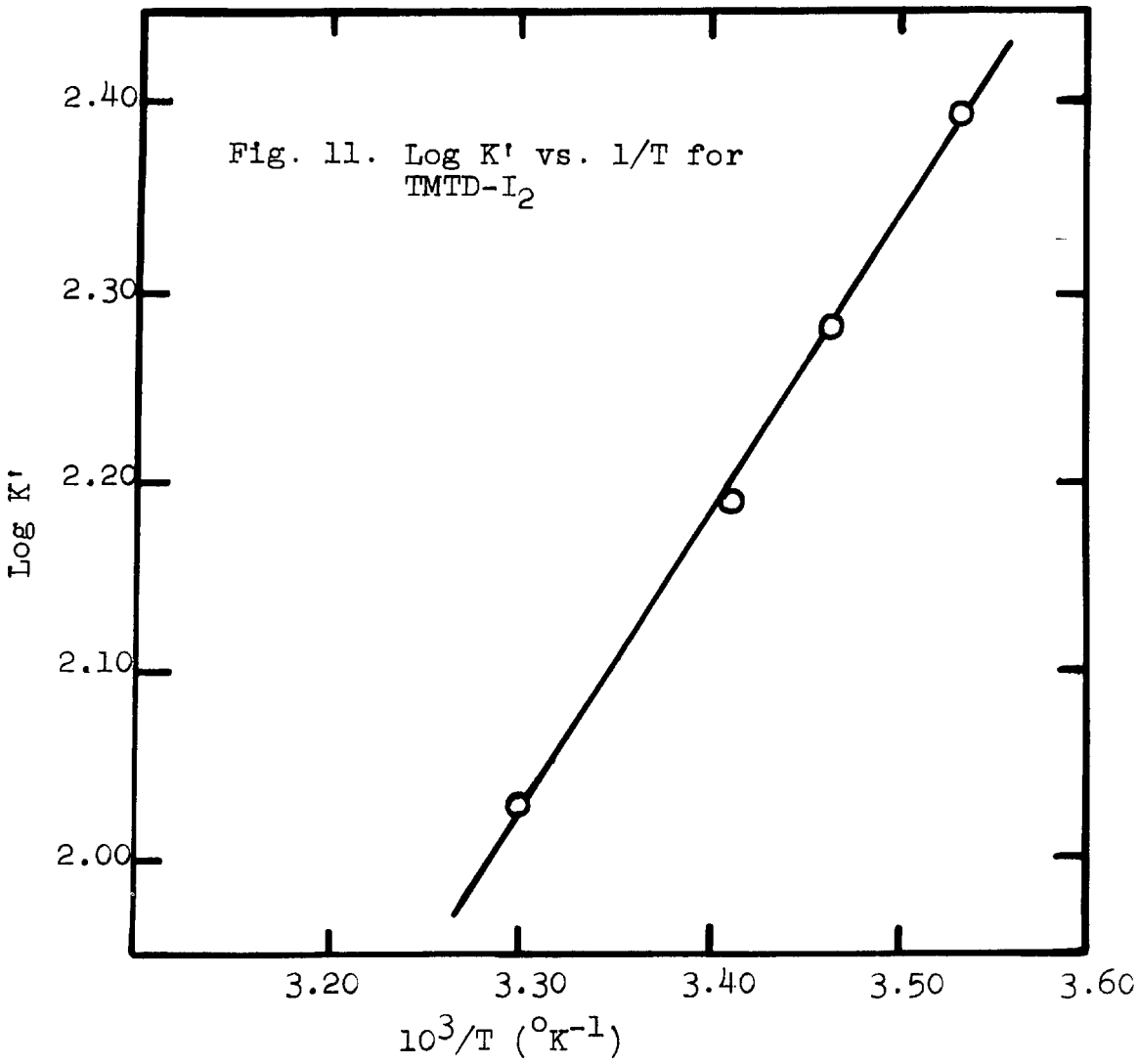


Fig. 11. Log K' vs. 1/T for TMTD-I_2

TABLE III. Summary of results for TMTD-I_2 (354 mμ)
K, ε obtained by Liptay analysis
Thermodynamic data based on the values of K'

Temp.(°C)	K_1(liter/mole)	K_2(liter/mole)	ϵ_c(liter/mole-cm.)
30.0	112 ± 35	111	3.17 x 10^4
20.0	151 ± 19	152	3.36
15.4	195 ± 48	194	3.27
10.0	249 ± 33	249	3.29
			$\epsilon_{ave.}$ = (3.27 ± .08)

ΔH^o = -7.18 ± 0.62 kcal./mole

ΔS^o = -14.4 ± 2.1 e.u.

ΔG^o_{298} = -2.88 kcal./mole

based on the values of K_2: ΔH^o = -6.89 ± 1.26 kcal./mole
ΔS^o = -13.4 ± 4.3 e.u.)

enthalpy shows smaller error limits when using K'.

D. TMTM-I_2

The TMTM-I_2 complex has an absorbance maximum at about 326-8 mμ in CCl_4 (Figure 12) although it appears as a shoulder in the unresolved spectrum. This system was studied at 10, 15, 20, and 30°C and in a concentration range of 0.4-2.5 x 10^{-4}M TMTM and 0.3-1.3 x 10^{-3}M I_2. The data are reported in Table XX and are plotted in Figure 13. The log K' vs. 1/T plot is shown in Figure 14.

Considerable experimental difficulty was encountered with this system. The major problem was in the apparent instability of TMTM in solution on exposure to light. Of secondary concern was the instability of some mixtures on standing, similar to that encountered with TMTD-I_2. Both problems were resolved by keeping the solutions in amber bottles for the duration of the run. Even then, more scatter than usual was observed in the plots of these data. However, the plot of log K' vs. 1/T is reasonably good and the error in the thermodynamic values is comparable to that in the other systems (Table IV).

E. MMDTC-I_2

The MMDTC-I_2 complex has an absorbance maximum at 347 mμ in CCl_4 (Figure 15). This system was studied at 10, 15, 20, and 30°C using the concentration ranges 0.8-4.1 x 10^{-4}M MMDTC and 0.55-1.7 x 10^{-3}M I_2. The data are presented in Table XXI and the modified Scott equation for

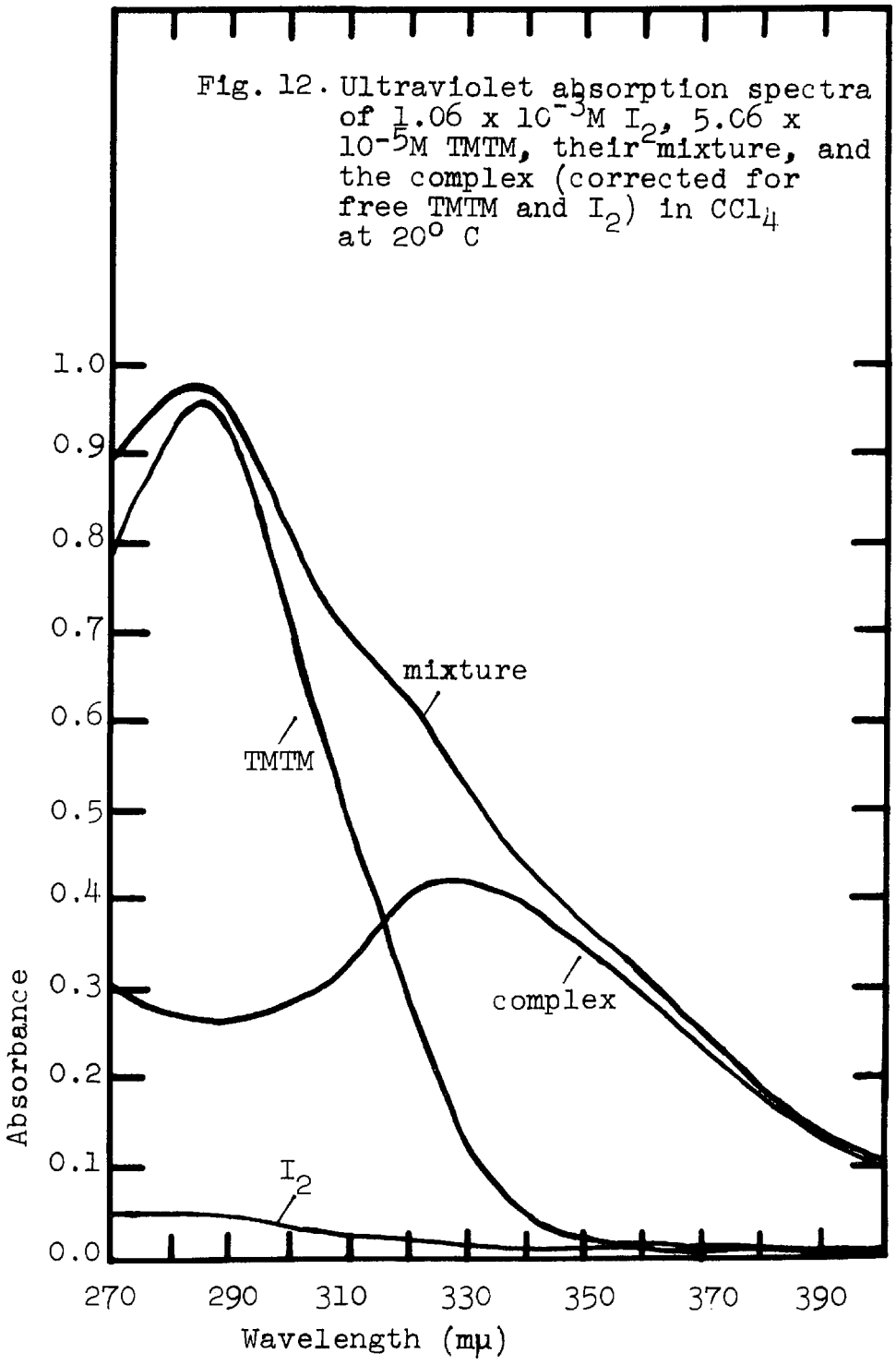


Fig. 12. Ultraviolet absorption spectra of 1.06×10^{-3}M I_2, 5.06×10^{-5}M TMTM, their mixture, and the complex (corrected for free TMTM and I_2) in CCl_4 at 20° C

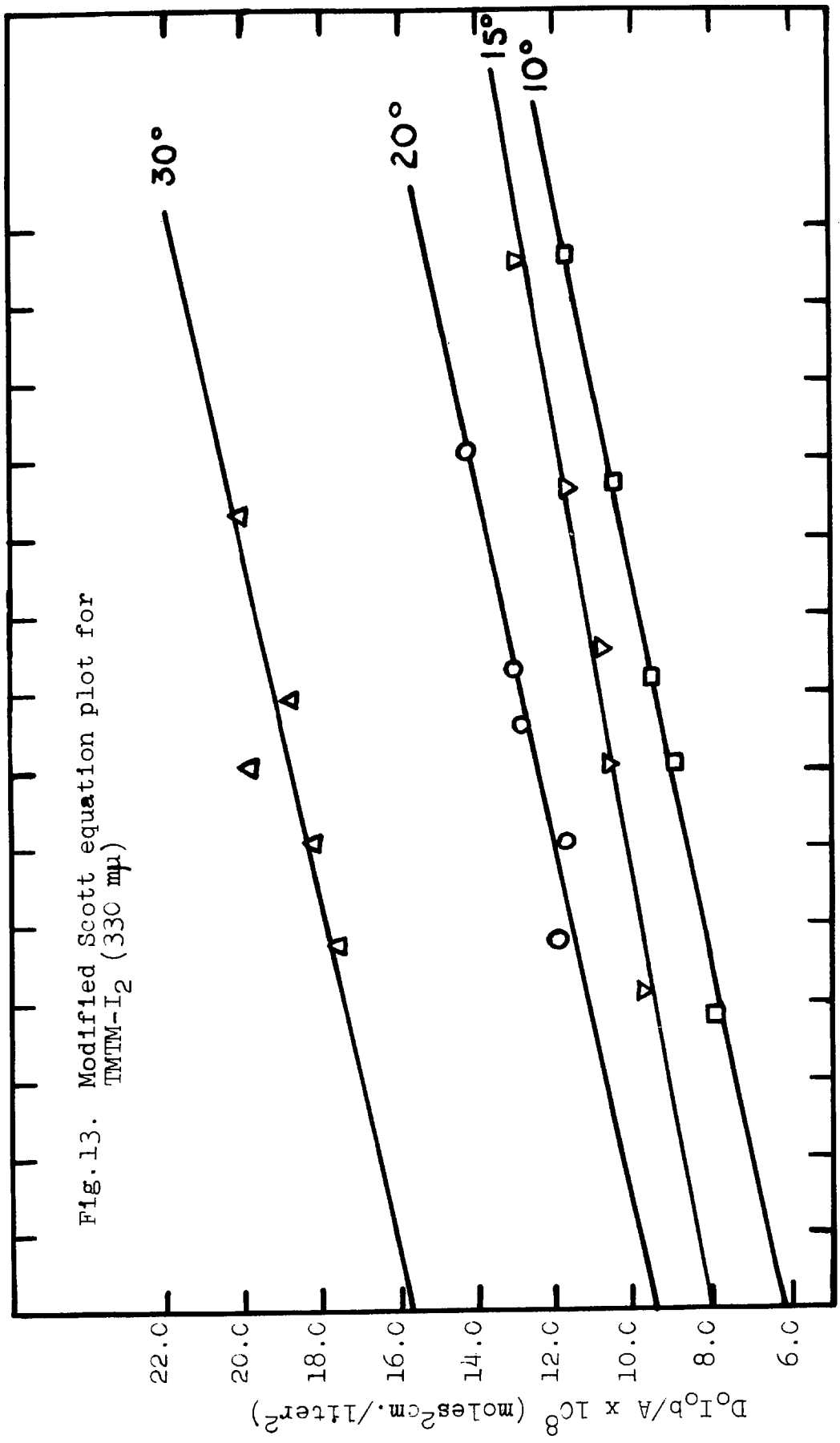


Fig. 13. Modified Scott equation plot for TMTM-I_2 (330 mμ)

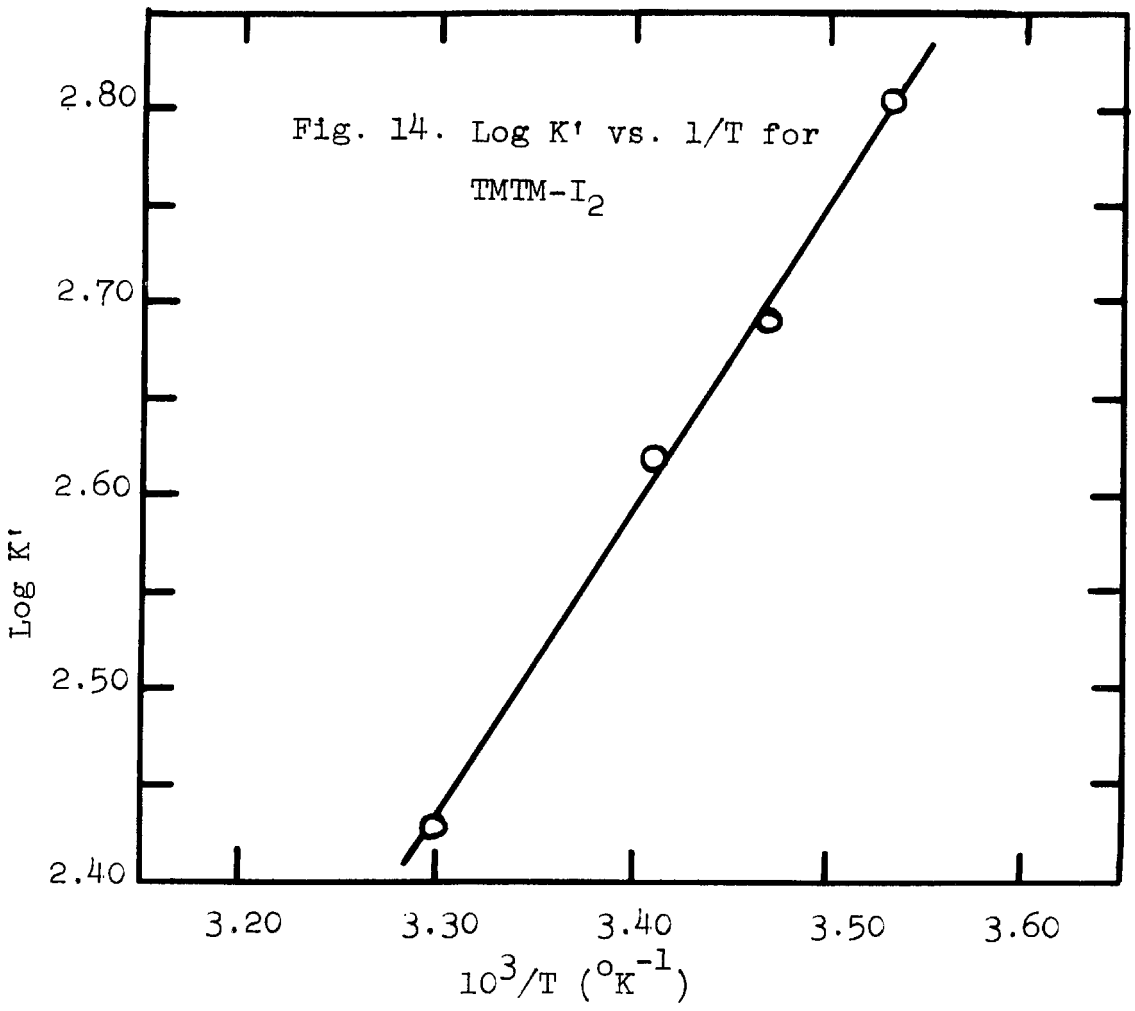


Fig. 14. Log K' vs. 1/T for TMTM-I_2

TABLE IV. Summary of results for TMTM-I_2 (330 mμ)
K, ε obtained by Liptay analysis
Thermodynamic data based on the values of K'

Temp(^oC)	K_1(liter/mole)	K_2(liter/mole)	ϵ_c(liter/mole-cm.)
30.0	279 ± 215	287	2.58×10^4
20.0	447 ± 148	433	2.66
15.4	438 ± 80	443	3.06
10.0	634 ± 59	647	2.73

$\epsilon_{ave.} = (2.76 \pm .22)$

$\Delta H^o = -7.30 \pm 0.66$ kcal./mole

$\Delta S^o = -13.0 \pm 2.3$ e.u.

$\Delta G^o_{298} = -3.44$ kcal./mole

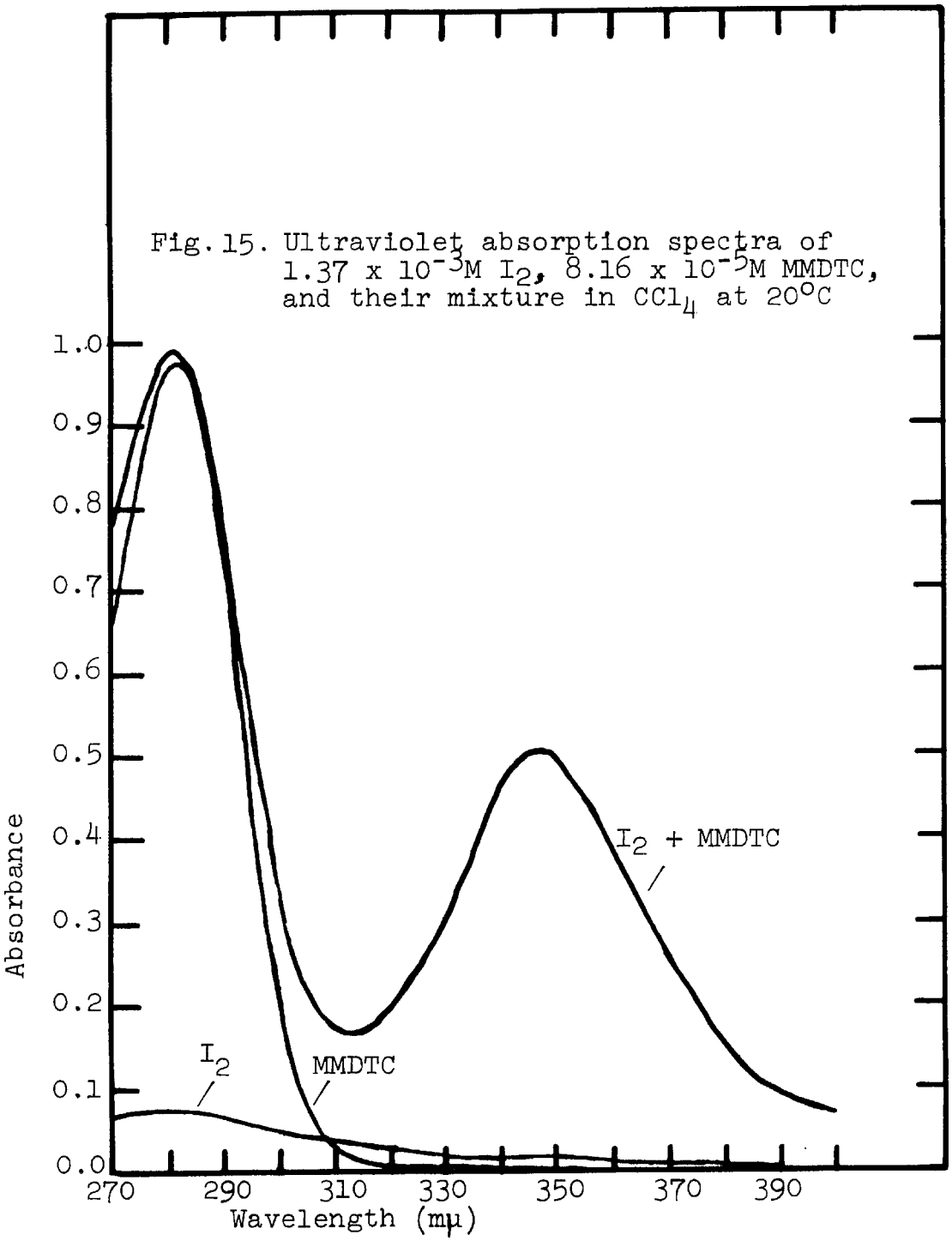


Fig. 15. Ultraviolet absorption spectra of 1.37×10^{-3}M I_2, 8.16×10^{-5}M MMDTC, and their mixture in CCl_4 at 20°C

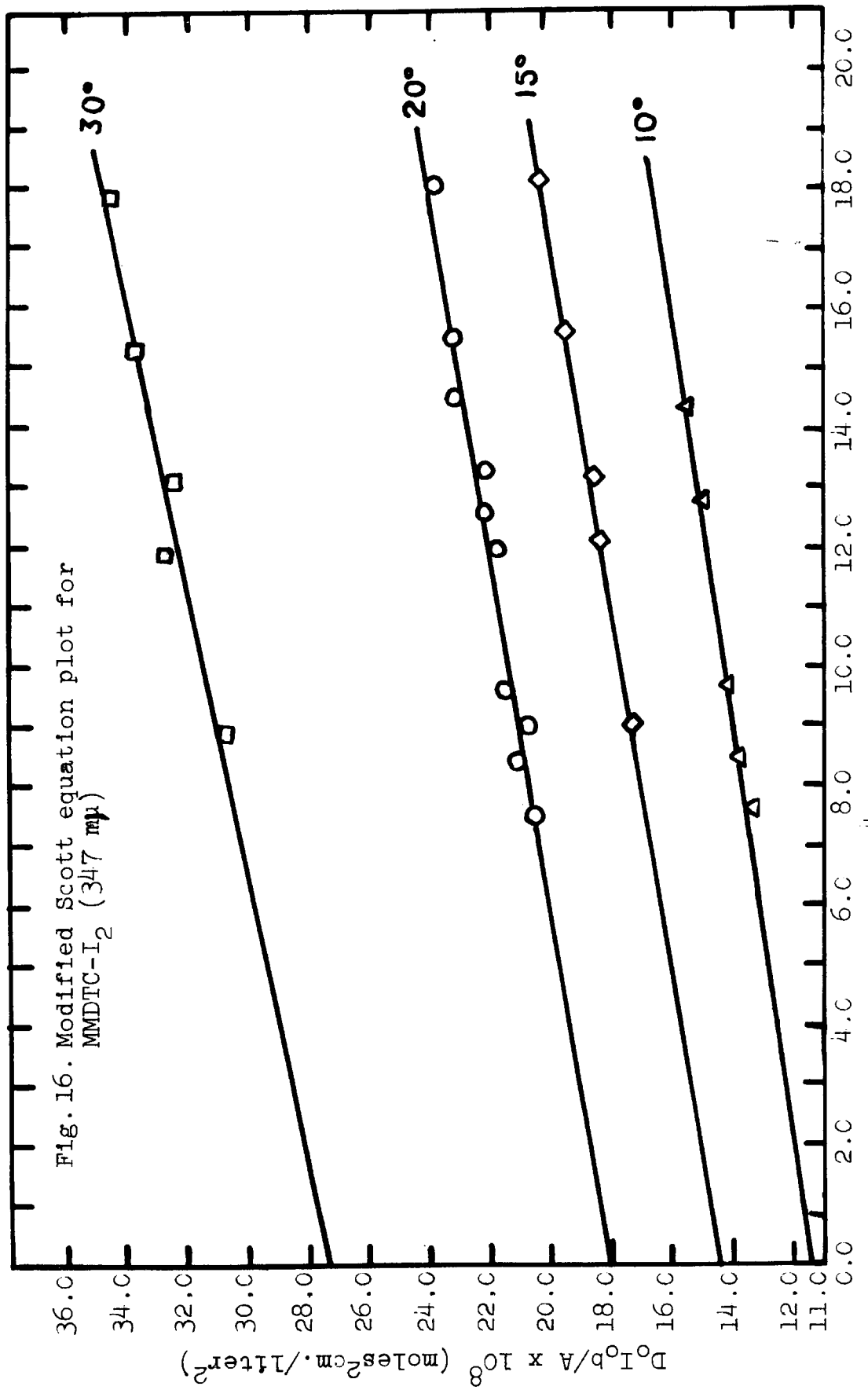


Fig. 16. Modified Scott equation plot for MMDTC-I_2 (347 mμ)

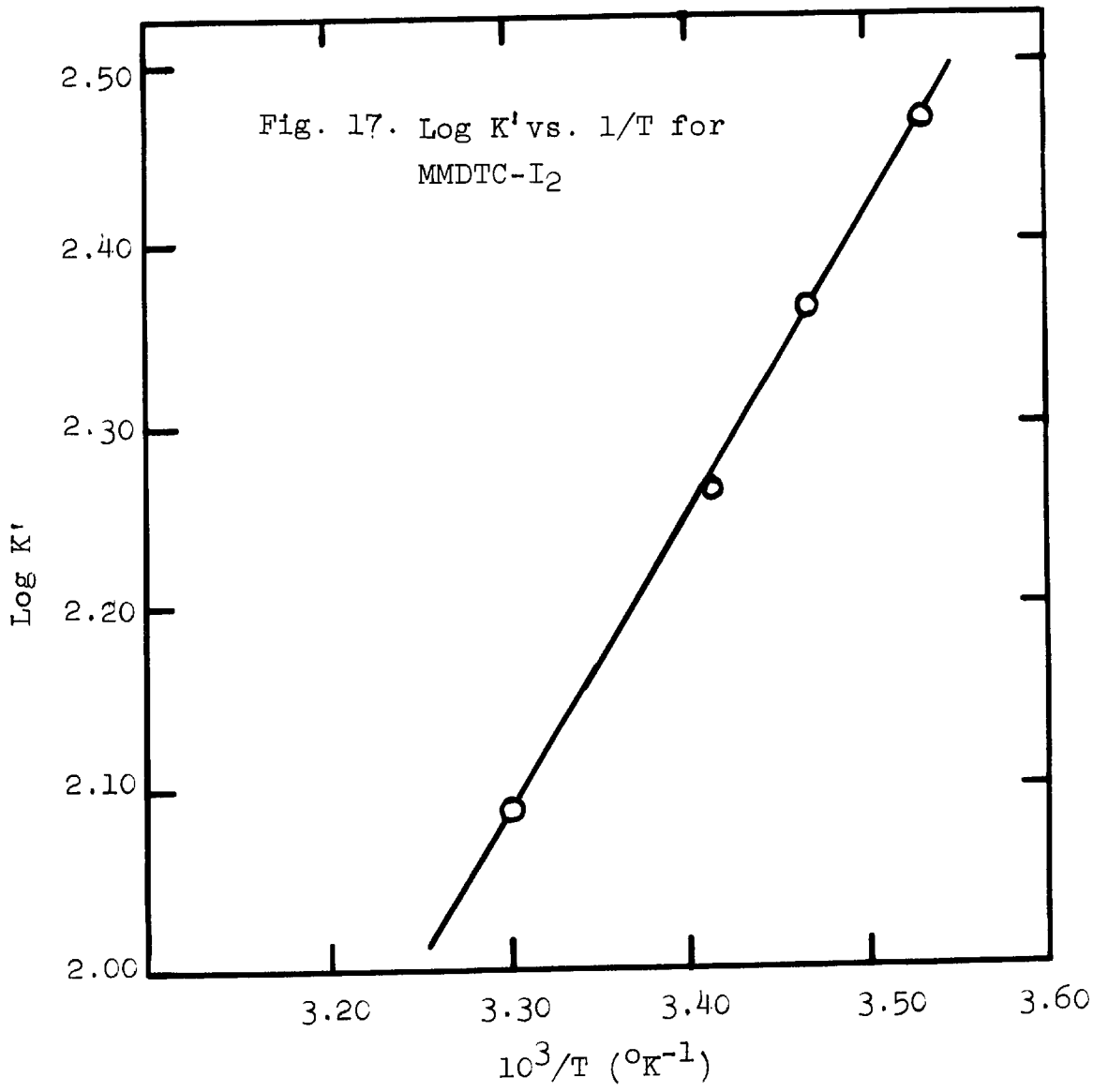


Fig. 17. Log K' vs. 1/T for MMDTC-I_2

TABLE V. Summary of results for MMDTC-I_2 (347 mμ)

K, ε obtained by Liptay analysis
Thermodynamic data based on the values of K'

Temp(^oC)	K_1(liter/mole)	K_2(liter/mole)	ϵ_c(liter/mole-cm.)
30.0	150 ± 26	149	2.46×10^4
20.0	183 ± 28	182	3.03
15.4	232 ± 36	230	3.03
10.0	263 ± 58	255	3.45
			$\epsilon_{ave.} = (2.99 \pm .44)$

$\Delta H^o = -7.53 \pm 0.36$ kcal./mole
$\Delta S^o = -15.3 \pm 1.2$ e.u.
$\Delta G^o_{298} = -2.97$ kcal./mole

this system is plotted in Figure 16. The log K' vs. 1/T plot is shown in Figure 17.

The results for this system are summarized in Table V. These mixtures did not exhibit the decomposition shown in the studies on TMTD and TMTM. On the contrary, they seemed quite stable even at the higher concentrations required to do a study in the visible region. A preliminary visible study of the MMDTC-I_2 system in CCl_4 showed the iodine absorption maximum shifted to around 450-460 mμ and an isosbestic point was observed at 508 mμ. The latter result is support for the existence of only a 1:1 complex even at the higher concentrations.

F. DMTA-I_2

The DMTA-I_2 complex has a primary absorption band at about 310 mμ and a secondary absorption that appears as a shoulder at about 340 mμ (Figure 18). Mixtures of DMTA (2.0-16.8 x 10^{-5}M) and I_2 (0.4-8.6 x 10^{-4}M) were investigated at 5, 10, 20, and 30°C at both 310 and 340 mμ. The data for this system are presented in Tables XXII and XXIII, and the modified Scott plots are shown in Figures 19 (310 mμ) and 21 (340 mμ). The corresponding log K' vs. 1/T plots are given in Figures 20 and 22.

A summary of results for this system at 310 mμ is presented in Table VI. These results are in good agreement with those of Drago, et. al.(16). He reports $K_{25°}$ = 1190 ± 40 liter/mole, and ΔH° = -9.5 ± 1.5 kcal./mole for a study of DMTA-I_2 in CCl_4 in the visible region.

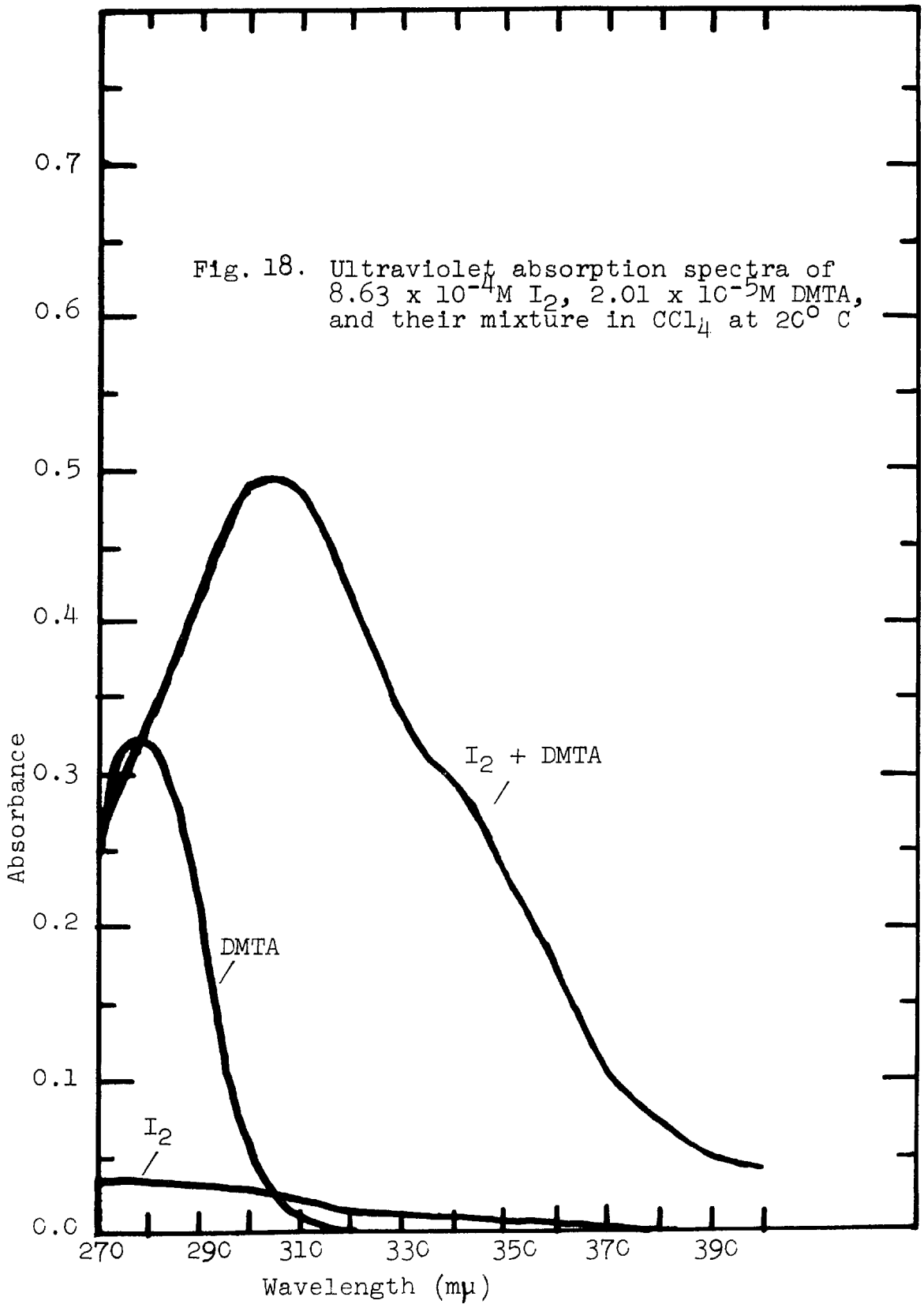


Fig. 18. Ultraviolet absorption spectra of 8.63×10^{-4}M I_2, 2.01×10^{-5}M DMTA, and their mixture in CCl_4 at 20° C

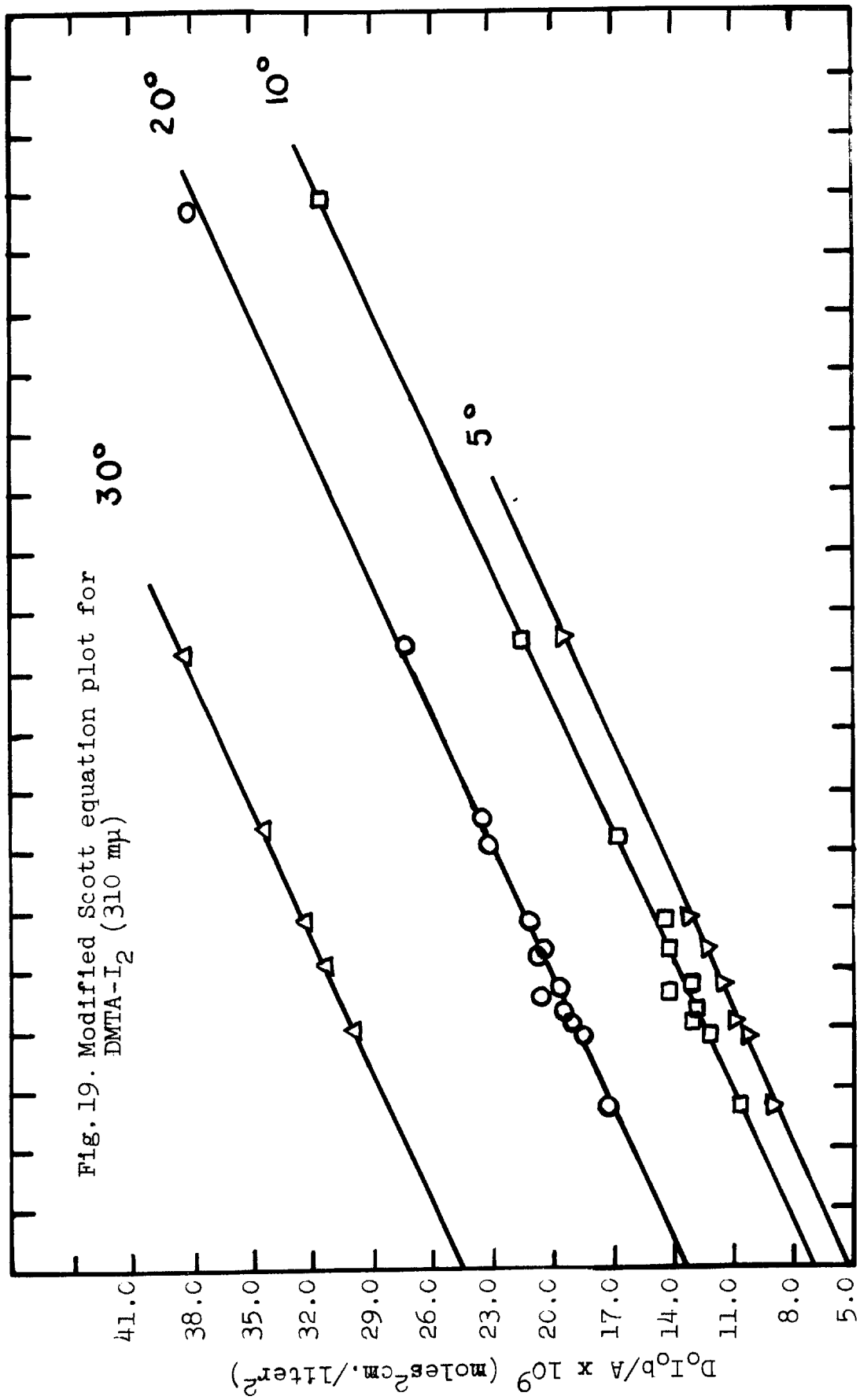


Fig. 19. Modified Scott equation plot for DMTA-I_2 (310 mμ)

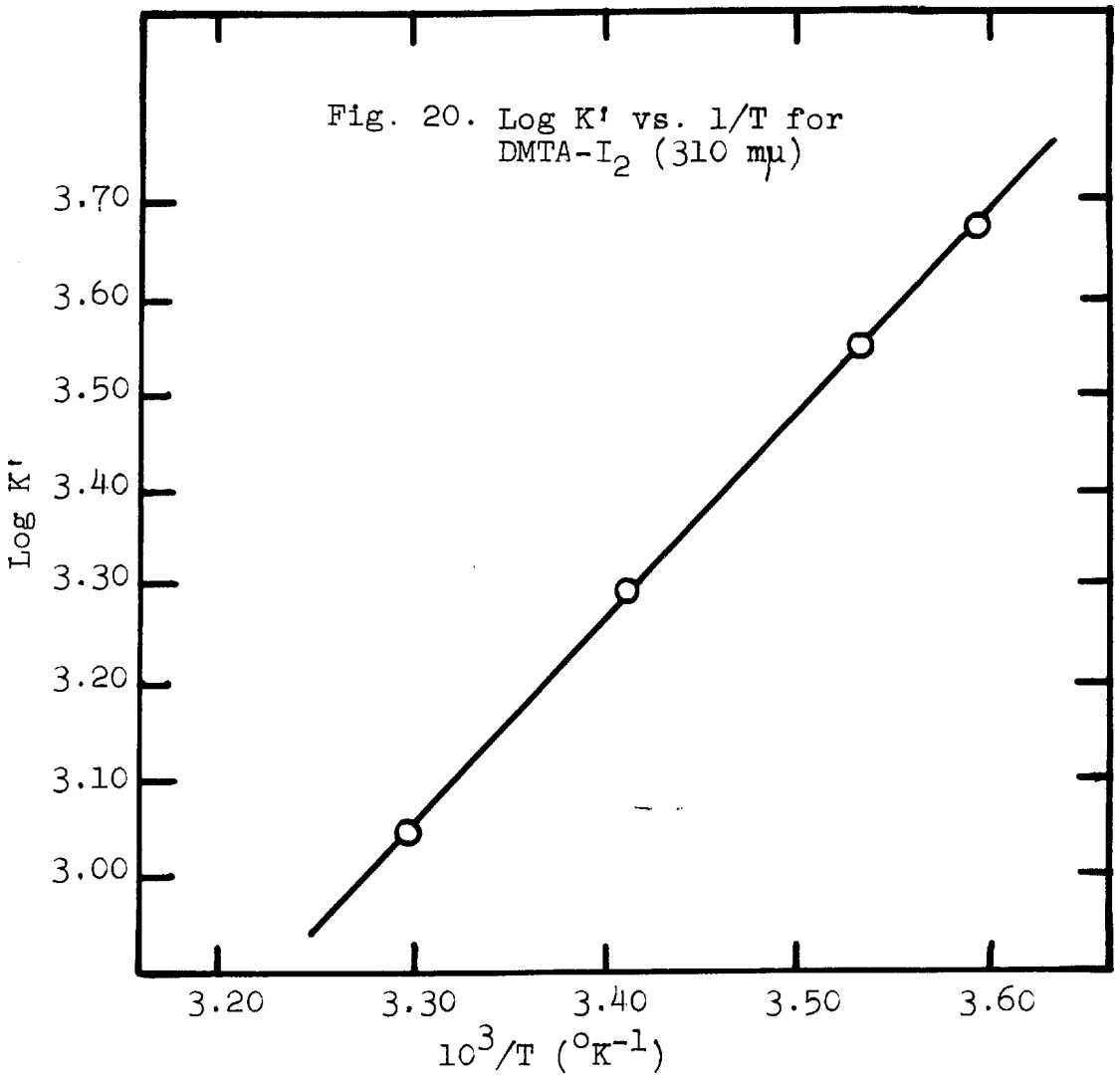


Fig. 20. Log K' vs. 1/T for DMTA-I_2 (310 mμ)

TABLE VI. Summary of results for DMTA-I_2 (310 mμ)

K, ε obtained by Liptay analysis
Thermodynamic data based on the values of K'

Temp(°C)	K_1(liter/mole)	K_2(liter/mole)	ϵ_c(liter/mole-cm.)
30.0	1090 ± 40	1120	3.64×10^4
20.0	2040 ± 90	1990	3.64
10.0	3820 ± 270	3540	3.70
5.0	4840 ± 330	4780	3.65

$\epsilon_{ave.} = (3.66 \pm .03)$

$\Delta H^o = -9.77 \pm 0.37$ kcal./mole

$\Delta S^o = -18.3 \pm 1.3$ e.u.

$\Delta G^o_{298} = -4.32$ kcal./mole

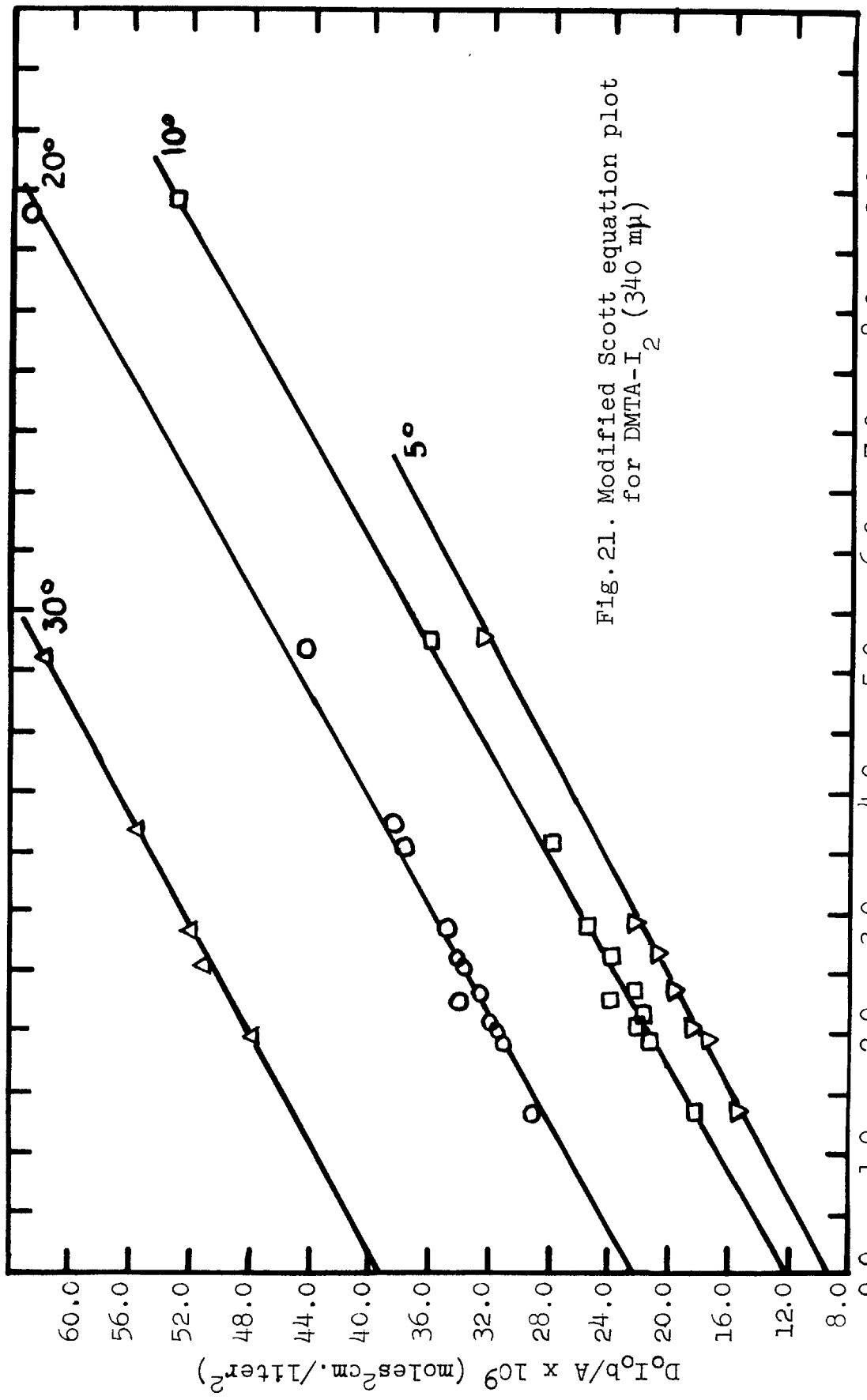


Fig. 21. Modified Scott equation plot for DMTA-I_2 (340 mμ)

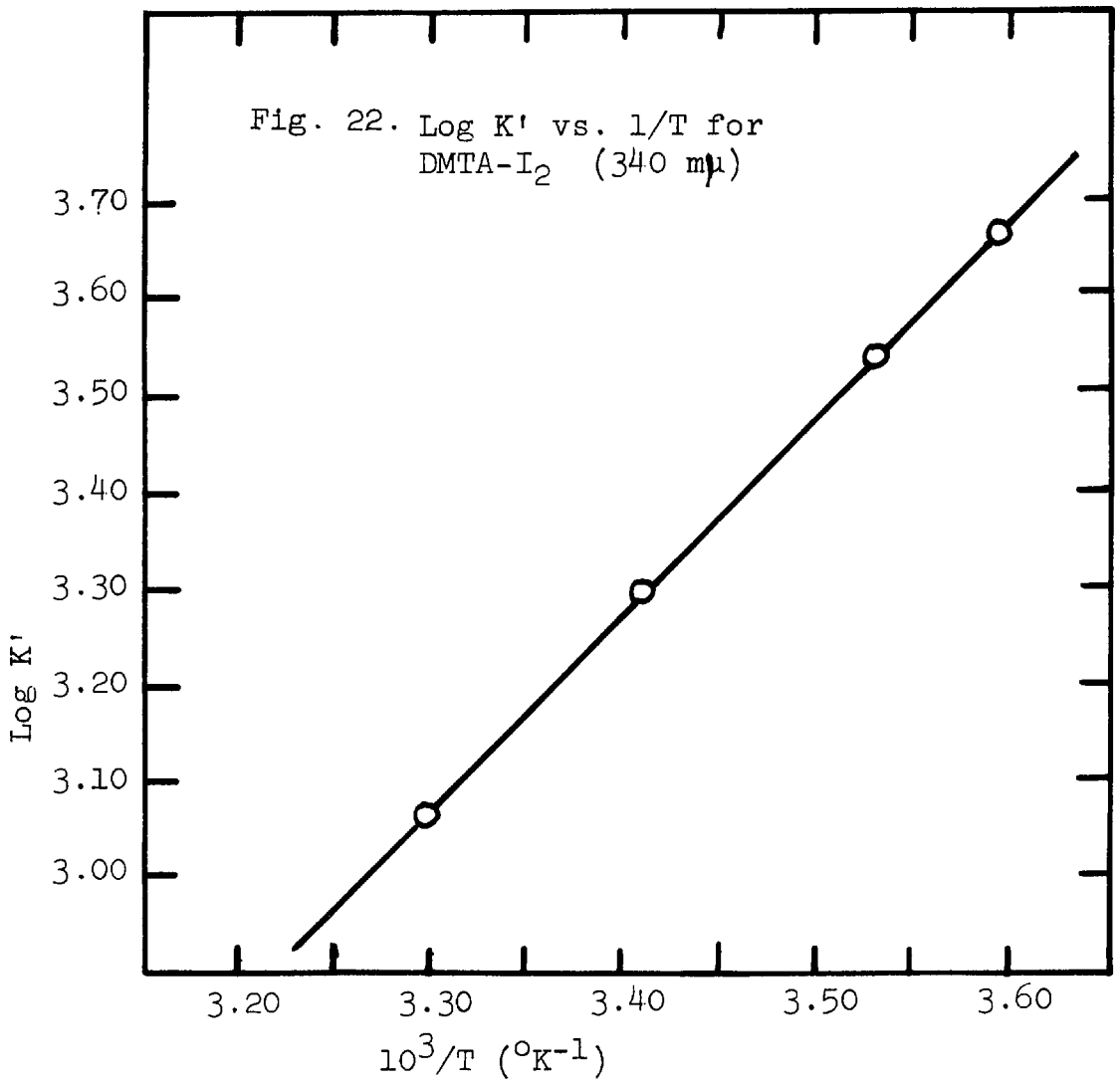


Fig. 22. Log K' vs. 1/T for DMTA-I_2 (340 mμ)

TABLE VII. Summary of results for DMTA-I_2 (340 mμ)

K, ϵ obtained by Liptay analysis
Thermodynamic data based on the values of K'

Temp.(°C)	K_1(liter/mole)	K_2(liter/mole)	ϵ_c(liter/mole-cm.)
30.0	1120 ± 70	1150	2.20 x 10^4
20.0	2010 ± 120	1970	2.21
10.0	3720 ± 230	3450	2.19
5.0	4790 ± 330	4740	2.14
			$\epsilon_{ave.}$ = (2.19 ± .03)

ΔH^o = -9.29 ± 0.14 kcal./mole

ΔS^o = -16.6 ± 0.5 e.u.

ΔG^o_{298} = -4.34 kcal./mole

The summary of results from the present study for DMTA-I_2 at 340 mμ is presented in Table VII. The similarity in stability constants and thermodynamic data between the studies at 310 mμ and 340 mμ suggest that both absorption bands arise from the same complex. A single complex is also suggested by the lack of any systematic deviations in the Liptay analysis as a function of wavelength (300-360 mμ).

In order to interpret the two absorption bands, ultraviolet spectra of several DMTA-I_2 mixtures were resolved in the following manner. For any given solution, equilibrium concentrations of DMTA and iodine were calculated from their initial concentrations and the stability constant at 20°C. The absorbances corresponding to uncomplexed DMTA and I_2 were then subtracted from the absorption spectrum of the mixture to give the curve due to the complex alone. A typical spectrum is shown in Figure 23 (Curve A), plotted on a linear frequency scale.

In order to further resolve the spectrum into components, two assumptions were made. The major band was assumed to be symmetrical with respect to frequency, and the minor band was assumed to have negligible absorbance below 310 mμ. Subtracting the symmetrical major band (Curve B, Figure 23) from the total absorbance (Curve A) produced a distinct maximum (Curve C). Although several approximations had to be made, the result gives reasonable evidence that an absorption maximum appears around 340-

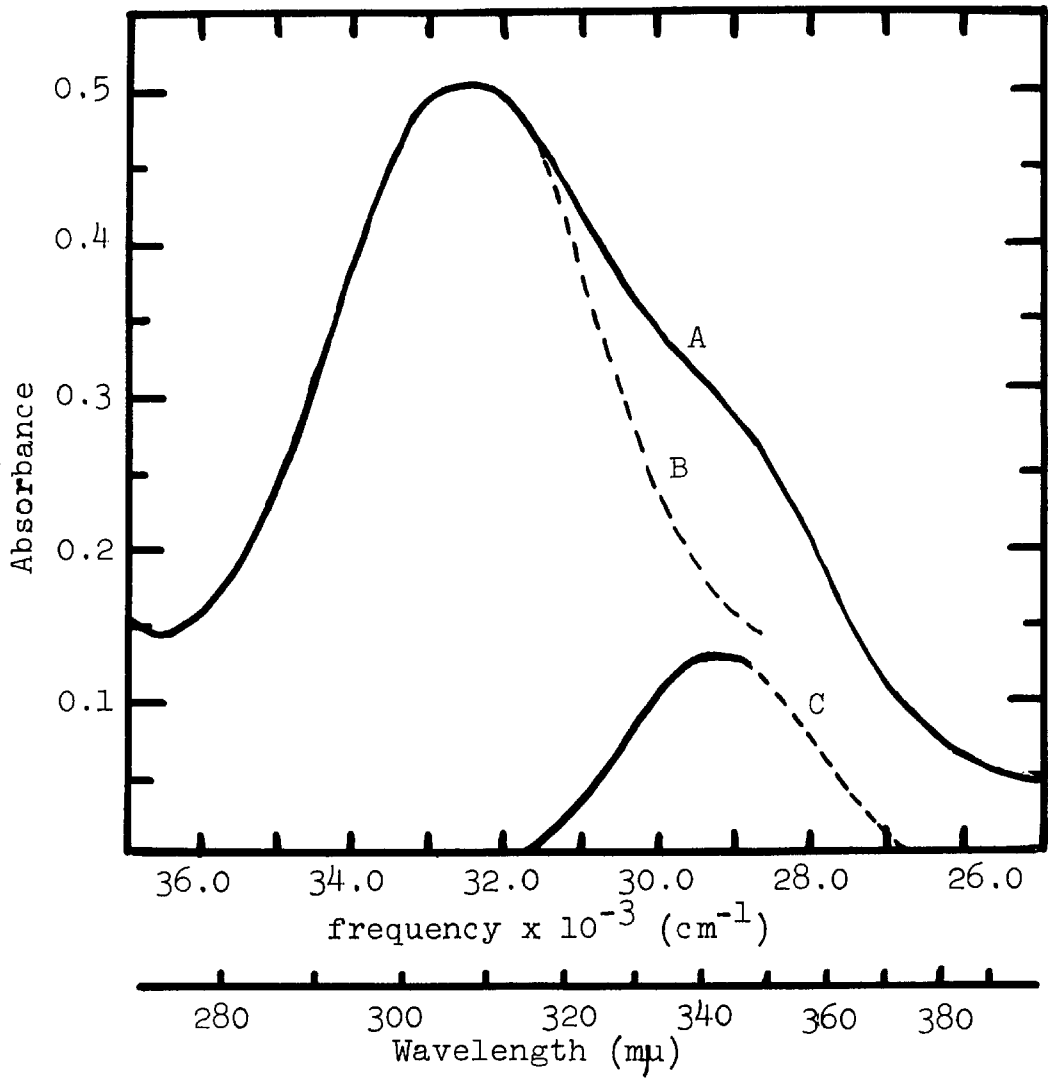


Fig.23. Resolution of DMTA-I_2 ultraviolet absorption:
A) Absorption of complex (corrected for free DMTA and free I_2)
B) Extrapolation of major band (mirror image of high energy side)
C) Result of subtracting B from A

Concentrations at 20° C:
Initial DMTA = 6.70×10^{-5}M
Initial I_2 = 1.44×10^{-4} M
equilibrium complex = 1.37×10^{-5}M

350 mμ for DMTA-I_2 mixtures in CCl_4. The maximum for the primary absorption falls around 307-8 mμ.

Six DMTA-I_2 solutions were resolved in a similar manner and a modified Scott equation analysis was done at both 307 and 340 mμ. The data and results of this study are shown in Table VIII. The equilibrium constants for the two bands are in reasonable agreement with one another and with the constants obtained previously (1990 l./mole at 310 mμ and 1970 l./mole at 340 mμ), supporting the original notion that both bands arise from the same complex.

The related thioacetamide (THIA)-iodine charge-transfer system has been studied in methylene chloride (CH_2Cl_2) and no secondary absorption band was reported (17). DMTA-I_2 shows the same absorption pattern in CH_2Cl_2 as it did in CCl_4, with slight blue-shifts (to about 304 mμ and about 335 mμ). In order to see if the THIA-I_2 system had a secondary absorption band also, the same resolution technique was applied to four solutions at 20°C (using a K of 10,700 liter/mole obtained from a modified Scott equation plot).

Figure 24 and Table IX show the results of the resolution of the ultraviolet absorption of THIA-I_2. A small, but apparent absorption band was located with a maximum around 320-325 mμ, in addition to the main band at around 295-6 mμ. The equilibrium constants are in good agreement with each other and with the data of Lang (17, K_{20}° calculated from his data is 11,100 liter/mole). The molar

TABLE VIII. Data and results for the resolution of the DMTA-I_2 ultraviolet absorption in CCl_4 at 20°C

$D_o \times 10^5$ (mole/liter)	$I_o \times 10^4$ (mole/liter)	$A_{corr.}$ 307 mμ	$A_{res.}$ 340 mμ
6.70	1.44	0.505	0.130
7.81	6.95	1.640	0.389
6.70	2.88	0.864	0.207
5.70	4.63	0.987	0.233
5.70	2.32	0.636	0.162
2.01	8.63	0.470	0.105

for 307 mμ:

$K = 1960 \pm 140$ liter/mole

$\epsilon = 37{,}500$ liter/mole-cm.

for 340 mμ:

$K = 2760 \pm 580$ liter/mole

$\epsilon = 7570$ liter/mole-cm.

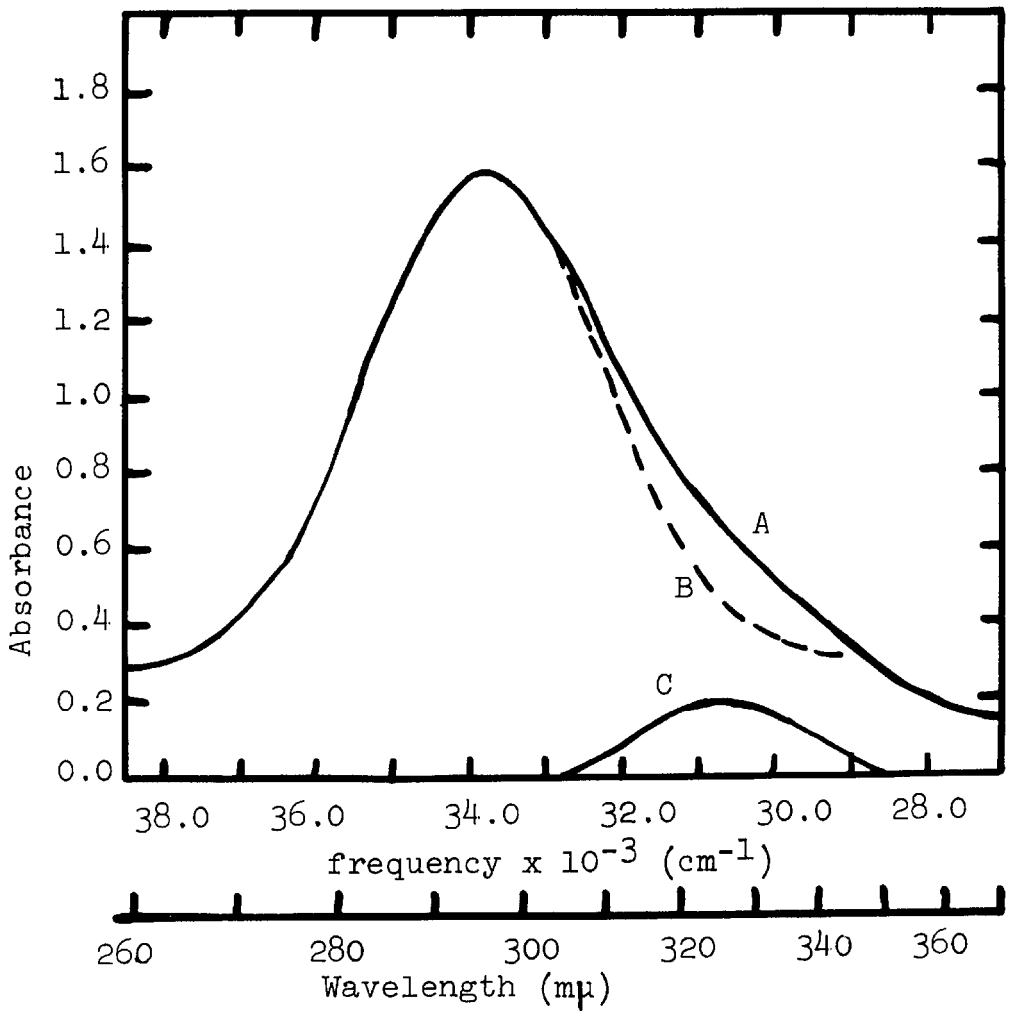


Fig. 24. Resolution of THIA-I_2 ultraviolet absorption:
A) Absorption of complex (corrected for free THIA and I_2
B) Extrapolation of major band (mirror image of high energy side)
C) Result of subtracting B from A

Concentrations at 20° C;
Initial THIA = 6.47×10^{-5} M
Initial I_2 = 1.38×10^{-4} M
equilibrium complex = 3.41×10^{-5} M

TABLE IX. Data and results for the resolution of the THIA-I_2 ultraviolet absorption in CH_2Cl_2 at 20°C

$D_o \times 10^5$ (mole/liter)	$I_o \times 10^5$ (mole/liter)	$A_{corr.}$ 295 mμ	$A_{res.}$ 325 mμ
6.47	6.92	1.035	0.130
6.47	9.69	1.295	0.145
6.47	13.8	1.590	0.200
6.47	27.7	0.479	0.059

for 295 mμ:

$K = 11{,}500 \pm 1600$ liter/mole

$\epsilon = 45{,}500$ liter/mole-cm.

for 325 mμ:

$K = 12{,}300 \pm 7380$ liter/mole

$\epsilon = 5340$ liter/mole-cm.

extinction coefficient of the 295 mμ band is also in reasonable agreement with that of Lang (~48,000 l./mole-cm.). The extinction coefficient of the secondary band is of the order of magnitude of that found for DMTA-I_2.

The main absorption band in both the DMTA- and THIA-I_2 cases is probably a charge-transfer band because it cannot be attributed to any transition of the isolated donor or acceptor, and it is also extremely intense. In addition, the position of this band is in the same region as those of the high intensity absorptions in related iodine systems (e.g., thiourea in CH_2Cl_2 at 298 mμ (17) and methylthioacetamide in CH_2Cl_2 at 296 mμ (18)).

There are two reasonable explanations for the appearance of the second absorption band in these mixtures. The first is that two charge-transfer bands exist, involving electrons from different energy levels in the donor. The second is that the minor band is due to an internal transition in the complexed donor.

If two distinct charge-transfer bands occur in these systems, it seems reasonable to expect that their origin would be from the two most easily excited energy levels. These two energy levels are probably the sulfur non-bonded "n" electron level and the N-C-S "π" electron level since the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions are the lowest energy transitions, in that order (18,68,69). However, if the intense charge-transfer band (~300 mμ) involves the lowest energy electron in the donor, as seems likely, then any

other transition from the donor to the acceptor must appear at a shorter wavelength. Since the minor band appears at a longer wavelength, the first possibility mentioned above probably is not valid.

If, on the other hand, the second absorption band is due to an internal transition in the complexed donor, it is tempting to suggest that the $n \rightarrow \pi^*$ transition in DMTA ($\lambda_{max} \sim 360$ mμ, $\epsilon_{max} \sim 70$ l./mole-cm. in CCl_4) or in THIA ($\lambda_{max} \sim 356$ mμ, $\epsilon_{max} \sim 40$ l./mole-cm. in CH_2Cl_2) has been blue-shifted and intensified by formation of the iodine complex. However, the apparent intensity of the secondary bands (around 5,000-7,000 l./mole-cm.), even allowing for sizable error in the analysis, seems quite high for an "$n \rightarrow \pi^*$" transition. But it would not be unreasonable to imagine that complexation perturbs considerably the antibonding molecular orbitals of the donor. Perhaps perturbation of the π^* energy level causes the $\pi \rightarrow \pi^*$ blue shift observed by Lang for the thioacetamide-iodine interaction (17), and a similar effect alters the $n \rightarrow \pi^*$ absorption. The increased intensity of the secondary band may be due to the transition being more allowed for the perturbed than the unperturbed π^*, or perhaps the new excited state can now mix with the excited state of the charge-transfer transition (17), and therefore borrow intensity from the more intense band.

Table X summarizes the approximate absorption band maxima of DMTA, THIA, and the corresponding I_2 complexes.

TABLE X. Approximate absorption band maxima of DMTA, THIA, DMTA-I_2, and THIA-I_2 in CH_2Cl_2.

Band	THIA $\pi \rightarrow \pi^*$	DMTA $\pi \rightarrow \pi^*$	THIA-I_2 CT	DMTA-I_2 CT	THIA-I_2 minor	DMTA-I_2 minor	THIA $n \rightarrow \pi^*$	DMTA $n \rightarrow \pi^*$
λ (mμ)	268[a,b]	272[a]	296[a,b]	304[a]	~325[a]	~335[a]	~356[b]	~360[c]
E (kcal./mole)	106.6	105.0	96.5	94.0	~87.9	~85.3	~80.3	~79.4
ΔE (kcal./mole)			CT maxima 2.5		minor bands ~2.6	THIA "blue-shift" ~7.6	DMTA "blue-shift" ~5.9	

a) this research
b) reference 17
c) $n \longrightarrow \pi^*$ in CCl_4

If the $n \rightarrow \pi^*$ band can be thought of as being "shifted" in the complex, then there should be some correlation between the extent of shift and the strength of interaction. If one considers the possible errors involved, the difference between a ΔE of ~ 5.9 kcal./mole for the DMTA "blue-shift" and ~ 7.6 kcal./mole for the THIA "blue-shift" may not be meaningful. It is interesting to note that the ΔE between the DMTA-I_2 and THIA-I_2 charge-transfer maxima is approximately equal to the ΔE between the secondary absorptions in the complexes. This supports the idea that the corresponding bands in the two complexes have similar origins.

The above discussion suggests that similar secondary bands may be present in other related systems. Detailed analysis of the absorption bands of the other complexes was not made because their charge-transfer bands are at higher wavelengths, which would mask a second band. The TMTM-I_2 absorption (Figure 12) is rather broad, suggestive of overlapping bands, but its shape does not permit resolution of the spectrum with any reliability.

G. Discussion of Donor Site

Table XI summarizes the pertinent data obtained in this study for the 1:1 charge-transfer complexes of TETD, TMTD, TMTM, MMDTC, and DMTA toward iodine (much of the data is repeated in Table XII for comparison with related systems). All members of the series except DMTA show similar donor strengths (by comparing either K or ΔH) toward iodine, taking into consideration the error limits placed on the mean values. Apparently, a single donor site is prominent in these related compounds, and the different substituents have little effect on the overall strength of the donor. This is shown further by comparing the enthalpies of the iodine interactions with MMDTC, $(CH_3)_2N\text{-}C(S)\text{-}SCH_3$, ΔH^o = -7.5 kcal./mole, and with O-methyl-N-methylthiocarbamate (MMTC), $(CH_3)NH\text{-}C(S)\text{-}OCH_3$, ΔH^o = -7.3 kcal./mole, both listed in Table XII. The effect of the O-methyl or S-methyl groups on the donor strength of the molecule is unimportant, suggesting that neither of these is the prominent donor site. Therefore, the donor site for all of these compounds must be in the N-C=S group, and is probably the same site as in dimethylthioacetamide (DMTA).

It has been shown (31,35) that the oxygen is the primary donor site toward iodine in amides, $R'\text{-}C(O)\text{-}NR_2$. By analogy, it has been suggested (16,17) that the donor site in thioamides and related compounds should be the sulfur.

Both valence-bond resonance theory (17) and molecular

TABLE XI. Spectral and thermodynamic data* on the charge-transfer complexes of iodine with five thione donors in CCl_4 solvent

Donor[a]	λ(mμ)	ϵave. (l./mole-cm.)	K_{20° (l./mole)	$-\Delta G^\circ_{298}$ (kcal./mole)	$-\Delta H^\circ$ (kcal./mole)	$-\Delta S^\circ$ (e.u.)
TETD	356	38,000	182 ± 34	3.00	6.38 ± .80	11.4±2.7
TETD	460	2,740	281 ± 9	3.24	6.62 ± 1.11	11.3±3.8
TMTD	354	32,700	152 ± 19	2.88	7.18 ± .62	14.4±2.1
TMTM	330	27,600	433 ± 148	3.44	7.30 ± .66	13.0±2.3
MMDTC	347	29,900	182 ± 28	2.97	7.53 ± .36	15.3±1.2
DMTA	310	36,600	1990 ± 90	4.32	9.77 ± .37	18.3±1.3
DMTA	340	21,900[b]	1970 ± 120	4.34	9.29 ± .14	16.6±0.5

* errors calculated at 90% confidence level

a) Abbreviations:
TETD, tetraethylthiuram disulfide, $(C_2H_5)_2NC(S)SSC(S)N(C_2H_5)_2$

TMTD, tetramethylthiuram disulfide, $(CH_3)_2NC(S)SSC(S)N(CH_3)_2$

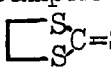
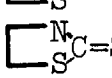
TMTM, tetramethylthiuram monosulfide, $(CH_3)_2NC(S)SC(S)N(CH_3)_2$

MMDTC, methyl dimethyldithiocarbamate, $(CH_3)_2NC(S)SCH_3$

DMTA, dimethylthioacetamide, $(CH_3)_2NC(S)CH_3$

b) This value represents two overlapping bands - see discussion of DMTA-I_2.

TABLE XII. Spectrophotometric and thermodynamic data for iodine charge-transfer interactions with substituted thiones

Donor[a]	Solv.	λ_{max} (mμ)	K_c (l./mole)	(t) (°C)	ΔH^o (kcal./mole)	ref.
TETD	CCl_4	356	182±34	(20°)	6.38±.80	*
TMTD	"	354	152±19	(20°)	7.18±.62	*
TMTM	"	326-8	433±148	(20°)	7.30±.66	*
MMDTC	"	347	182±28	(20°)	7.53±.36	*
DMTA	"	306-8	1990±90	(20°)	9.77±.37	*
DMTA	"	b	1190±40	(25°)	9.5±1.5	16
TMTU	"	b	8000±200	(25°)	10.5±0.5	16
THIA	CH_2Cl_2	296	12,000±900	(17°)	8.2±1.8	17
THIU	"	298	8,500	(20°)	9.6±1.0	17
thio-camphor	⬡	~305[c]	95	(25°)	11.0± 1	18
	"	b	45	(25°)	8.5± 1	18
	$CHCl_3$	~308	1406	(25°)	10.0± 1	18
MTA	CH_2Cl_2	~296	540	(25°)	8.4± 1	18
MMTC	⬡	~304	8120	(27°)	7.3± 1	18
TMTU	$CHCl_3$	334	13,560	(25-26°)	9.5± 1	36
DETU	"	304	15,520	(25-26°)	14.4± 1	36

*) Data from this research.

a) Abbreviations: (see also note a, Table XI)
TMTU, tetramethylthiourea, $(CH_3)_2NC(S)N(CH_3)_2$
THIA, thioacetamide, $H_2NC(S)CH_3$
THIU, thiourea, $H_2NC(S)NH_2$
MTA, methylthioacetamide, $(CH_3)HNC(S)CH_3$
MMTC, O-methyl-N-methylthiocarbamate, $(CH_3)HNC(S)OCH_3$
DETU, diethylthiourea, $(C_2H_5)HNC(S)NH(C_2H_5)$

b) No UV maximum reported; data from visible study.

c) UV maximum reported, but data from visible study.

orbital calculations (68) point to the sulfur as the site with the greatest amount of negative charge. In agreement with these theoretical views, electron release by the nitrogen toward the thiocarbonyl group has been shown by X-ray studies (52) and n.m.r. studies (16) to produce a high degree of double-bond character in the C-N bond. Related n.m.r. studies (16) of the C^{13}-H coupling constants of the N-methyl groups in DMTA showed that the electron donor ability of the nitrogen is considerably weaker than in dimethylamine or in N,N-dimethylaniline. In support of the above statements, which favor the sulfur over the nitrogen as the donor site, Lang (17) and Drago, et. al. (16), point out that thioamide-iodine interactions are stronger, rather than weaker, than the corresponding amine-iodine interactions; and are stronger, as expected, than sulfide-iodine interactions.

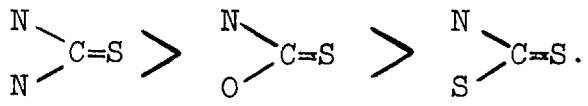
Bhaskar, Gasovi and Rao, used infrared data to support their argument of an iodine association with the sulfur in thioureas (36). They point out that the bands attributed largely to the C=S stretch decrease in frequency and increase in intensity upon addition of iodine; and, at the same time, bands assigned to N-C-N motions increase in frequency. Gerbier and Gerbier (85) also concluded from infrared studies on thioacetamide and related compounds that iodine coordinates to the sulfur.

Table XII lists all the data available on donor-iodine systems that are pertinent to the discussion of donor site

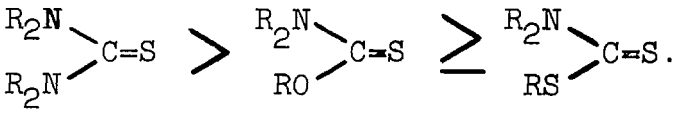
for thioamides and related species. It is important, however, to note some of the limitations of this type of compilation before comparing the data. As a general rule, the effects of solvent on the spectral and thermodynamic results for molecular complexes are large (92), and a great deal of latitude must be considered when comparing such data. Also, results obtained from different laboratories may not be in agreement either. For example, the equilibrium constants reported by two different laboratories for the thioacetamide (THIA)-iodine and methylthioacetamide (MTA)-iodine complexes, both in methylene chloride solvent, are very different, even though their enthalpies are quite similar. Also, results on the tetramethylthiourea (TMTU)-iodine complex in different solvents (and in different laboratories) disagree both in ΔH and in K.

The K's and ΔH's(Table XII) suggest the donor strength order toward iodine (in CCl_4) of TMTU > DMTA > MMDTC. This is the same order of donor strength found by Janssen (81) toward H^+ in aqueous H_2SO_4. Since he has shown (see Introduction, p. 13) that the donor site in his studies is the thiocarbonyl sulfur, it suggests that these donors might be interacting with iodine in a similar manner.

Janssen also has made theoretical calculations (68) on a series of thiones. His results for negative charge on the thiocarbonyl sulfur, and relative energy levels of the sulfur non-bonded n-electrons suggest a donor order of

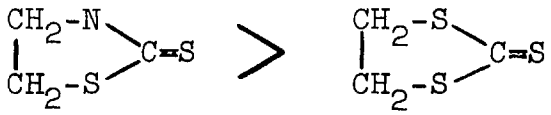


A similar order of donor strength toward iodine can be seen by considering the K's and ΔH's in Table XII for the series

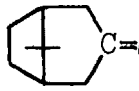


(TMTU, THIU) (MMTC) (MMDTC)

Janssen further predicts that $\overset{N}{S}\!>\!C\!=\!S$ should be a stronger donor than $\overset{S}{S}\!>\!C\!=\!S$. This is again shown by the relative donor strengths (K and ΔH) toward iodine of



(thiazolidine-2-thione) (ethylenetrithiocarbonate)

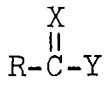
It is interesting to note that thiazolidine-2-thione (above) appears to be a much stronger donor than MMDTC, even though they contain the same hetero atoms. Also, both thiocamphor () and ethylenetrithiocarbonate (above) have large ΔH's and very small K's. These anomalies may be due to the cyclic structure of these three compounds. Tamres and Searles have discussed the effect of ring size on the donor ability of cyclic sulfides (30) and cyclic ketones (93) and have compared cyclic and non-cyclic structures. The orientation and association of

solvent molecules around the free and complexed species could well be different for cyclic and non-cyclic species, which probably affects the K and ΔH.

The strengths of interaction toward iodine of a series of thiones are collected in Table XIII, along with a related series of carbonyl compounds. The authors reporting these studies on carbonyl compounds all consider oxygen to be the donor site toward iodine. If the thiocarbonyl sulfur is interacting in the same manner, then substituent effects might be expected to show the same trend in both series. For example, the substitution of NR_2 groups enhances the strength of interaction in both series to approximately the same degree.

The relative effects of $N(CH_3)_2$, SCH_3, OCH_3, and CH_3 substitution on the donor strengths of C=S and C=O also may be compared. In both series, even with different "Y" groups, the increase in donor strength of the molecule due to the "R" substituent is $N(CH_3)_2 > SCH_3 > OCH_3$. The CH_3 group, however, falls above SCH_3 in the sulfur series, and below it in the oxygen series. This can be rationalized by considering that SCH_3 probably undergoes some π-interaction to override its slight tendency to attract electrons. This tends to make CH_3-C(O)-SCH_3 a slightly better donor through oxygen than CH_3-C(O)-CH_3. But π-bond formation by SCH_3 in NR_2-C(S)-SCH_3 detracts from the predominant effect of the NR_2 group and makes it a weaker donor than NR_2-C(S)-CH_3. This is in accord with the

TABLE XIII. Strengths of interaction of substituted carbonyl and thiocarbonyl compounds with iodine



=X	-R	-Y	$-\Delta H^{o}$ (kcal./mole)	Solv.	ref.
S	$N(CH_3)_2$	$N(CH_3)_2$	10.5	(CCl_4)	16
	CH_3	$N(CH_3)_2$	9.8	(CCl_4)	a
	CH_3	$NH(CH_3)$	8.4	(CH_2Cl_2)	18
	CH_3	NH_2	8.2	(CH_2Cl_2)	17
	SCH_3	$N(CH_3)_2$	7.5	(CCl_4)	a
	OCH_3	$NH(CH_3)$	7.3	(cyclohex.)	18
O	$N(CH_3)_2$	$N(CH_3)_2$	4.3	(CCl_4)	73
	$N(CH_3)_2$	CH_3	4.0	(CCl_4)	16
	SCH_3	CH_3	3.2	(CCl_4)	16
	OCH_3	CH_3	2.5	(CCl_4)	73
	CH_3	CH_3	2.5	(cyclohex.)	18
	CH_3	NH_2	4.6[b]	(CH_2Cl_2)	29

a) this research

b) $K_{22}^{o} = 0.61$ l./mole suggests that the $-\Delta H^{o}$ reported is rather high. K_{25}^{o} for CH_3-C(O)-SCH_3 for example, is 0.73 l./mole ($\Delta H^{o} = -3.2$ kcal./mole).

observation (35) that the barrier to rotation around the C-N bond in R_2N-C(O)-CH_3 is significantly reduced by substituting SCH_3 for CH_3.

Further support of the carbonyl and thiocarbonyl groups as the primary donor sites in the compounds listed in Table XIII comes from comparing the ΔH of either tetramethylthiourea, $(CH_3)_2N$-C(S)-$N(CH_3)_2$, or dimethylthioacetamide, $(CH_3)_2N$-C(S)-CH_3, with their oxygen analogs. The difference in ΔH in both cases of about 6 kcal./mole must be due to a change in donor atom. Similarly, comparison of the iodine and phenol complexes with carbonyl compounds and with the analogous thiocarbonyl species (16, and Table 2 of reference 18) showed the same reversal of donor strengths that is found for ethers and thioethers toward these acceptors. The sulfur compounds were found to be stronger donors than the oxygen analogs toward iodine, but the reverse was true toward phenol.

If the thiocarbonyl sulfur is the predominant donor site in all of the systems considered above, some difference in entropy might be expected between the donors which contain only one thiocarbonyl site and those which contain two identical sites (TETD, TMTD, TMTM). Assuming that the maximum effect of two identical sites is to increase the stability constant, K, by a factor of two, then the entropy difference (assuming, also, the same enthalpy) would be only Rln2, or about 1.4 e.u. This is well within the experimental error limits ($\pm$ 2-3 e.u.) of the method, so that such an effect would be masked.

II. CHARGE-TRANSFER INTERACTIONS OF COORDINATED LIGANDS

A. Introduction

The effect of coordination on the chemical reactivity of ligands has been the subject of many studies (94 and references therein, 95). Recently, however, some investigations have been directed toward formation of electron donor-acceptor adducts with coordination compounds. For example, several metallocenes (cyclopentadienyl-metal complexes) were found to form 1:1 molecular complexes (96, 97,98) with "π" acceptors such as tetracyanoethylene and p-chloranil. Complete electron transfer often resulted, however, to form salts, and in no case was there shown a charge-transfer interaction simply between ligand and acceptor.

Schrauzer and Mayweg (99) showed that adducts formed between dithio-α-diketone metal complexes ($\begin{matrix} R\text{-}C\text{-}S \\ \| \quad \diagdown \\ R\text{-}C\text{-}S \quad M \end{matrix}$) and nitrogen bases (e.g., pyridine) or olefins. The structure of these adducts was not established, but direct donation to the metal ion was suggested.

Forster and Goodgame studied adducts of iodine with coordinated isothiocyanate ligands (75). Although the iodine apparently attached to the ligand, the specific nature of the interaction was not shown.

The study reported in this section was undertaken to investigate the effects of coordination to metal ions on the charge-transfer properties of ligands. A suitable chelate ligand would have the general structure $X\begin{matrix}\nearrow D \\ \searrow D\end{matrix}$, where the D's represent electron donor sites coordinated to a metal ion, and X represents a donor site not coordinated to the metal ion. Thus, X could behave as a donor toward an external acceptor, A, with the interaction being affected by the nature of the metal ion.

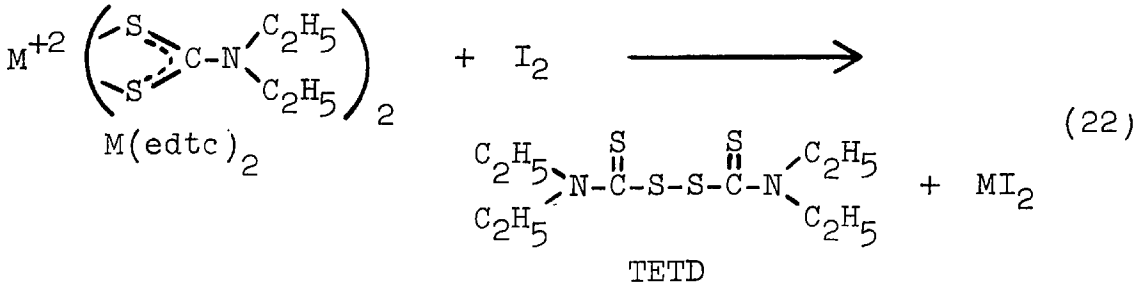
The "charge-transfer" interaction of X with A, studied spectrophotometrically, must have certain general properties. (1) The metal chelate should be stable and soluble in comparatively "inert" organic solvents such as chloroform or carbon tetrachloride (i.e., solvents which do not compete strongly for interaction with either the donor or the acceptor). (2) The donor-acceptor interaction should either produce a new band in an optically clear spectral region, or at least show a pronounced shift of one of the existing bands. (3) The interaction should be an easily reversible one.

B. Reactions of Some Metal Diethyldithiocarbamates with Iodine

Since the thiones in general are good electron donors (see Introduction), it was thought that coordinated dithiocarbamates (structure VIII) might still serve as donors, through the nitrogen, toward an external acceptor. These metal salts seemed promising because of their stability

and solubility in chloroform, so the interaction of iodine with several metal diethyldithiocarbamates was undertaken.

The mixture of iodine and mercuric diethyldithiocarbamate solutions did produce a new intense ultraviolet absorption band which was stable, was temperature dependent, and showed reversibility. However, a study of this system in the visible region showed that the iodine was being consumed, as evidenced by its loss of color. Detailed analysis of mixtures of iodine with the diethyldithiocarbamates (edtc) of mercury (II), lead (II), zinc (II), and cadmium (II) showed that the following reaction takes place.



$M^{+2}\left(S_2C\text{-}N(C_2H_5)_2\right)_2 + I_2 \longrightarrow (C_2H_5)_2N\text{-}C(=S)\text{-}S\text{-}S\text{-}C(=S)\text{-}N(C_2H_5)_2 + MI_2$ (22)

$M(edtc)_2$ TETD

The charge-transfer interaction observed in the ultraviolet study probably was due to the reaction product TETD forming a complex with excess iodine (see section IA, under Results and Discussion).

The extent to which this reaction (equation 22) is complete depends on the relative stabilities of the reactants and products. In the case of the zinc complex, the reaction does not go to completion. This is shown clearly by the photometric titration of iodine by $Zn(edtc)_2$

(Figure 25 and Table XIV). The mercury complex, on the other hand, produces a sharp end point by this method (Figure 26 and Table XV). The mercury, lead, and cadmium complexes can be titrated by iodine in chloroform to a sharp visual 1:1 end point (Table XVI), whereas this does not occur in the titration of the zinc complex.

The products of the reaction of $Pb(edtc)_2$ with iodine in chloroform were isolated and identified. The reaction produces a yellow precipitate which was identified as lead iodide by ultraviolet and infrared analyses. The ultraviolet spectrum of the precipitate in aqueous 4M potassium iodide was identical with that of a known sample of PbI_2 in the same medium (λ_{max} = 357 mμ, agrees with reference 101). The infrared spectra of the yellow precipitate and of PbI_2, both recrystallized from dimethylformamide, are also identical (Figure 27). It should be noted, however, that the infrared absorption bands of these compounds in the region 4000-600 cm^{-1} are probably due to coordinated dimethylformamide (102). Their similarity here is nevertheless a reasonable measure of identification. Further, quantitative isolation of the precipitate accounted for about 98% of the expected yield of PbI_2.

The chloroform-soluble product of the I_2-$Pb(edtc)_2$ reaction was isolated, and recrystallized from ethanol. It was identified as TETD by its infrared spectrum (103). The ultraviolet spectrum of the original chloroform solution was compared with that of a known sample of TETD and found

TABLE XIV. Photometric titration of iodine by zinc diethyldithiocarbamate, $Zn(edtc)_2$, in chloroform temp. = 22-23°C

conc. $Zn(edtc)_2$ (moles/liter)	moles $Zn(edtc)_2$ / mole I_2 [a]	Absorbance [b] at 510 mμ
0.00×10^{-4}	0.000	0.742
1.67	0.200	0.589
2.51	0.301	0.514
3.34	0.400	0.445
5.01	0.600	0.306
6.68	0.800	0.168
7.52	0.902	0.107
7.94	0.953	0.087
8.36	1.00	0.060
9.18	1.10	0.026
10.0	1.20	0.019
12.5	1.50	0.006

graphical end point (see Fig. 25) = 1.00 moles Zn/mole I_2

a) conc. $I_2 = 8.35 \times 10^{-4}$

b) path length = 1.00 cm.

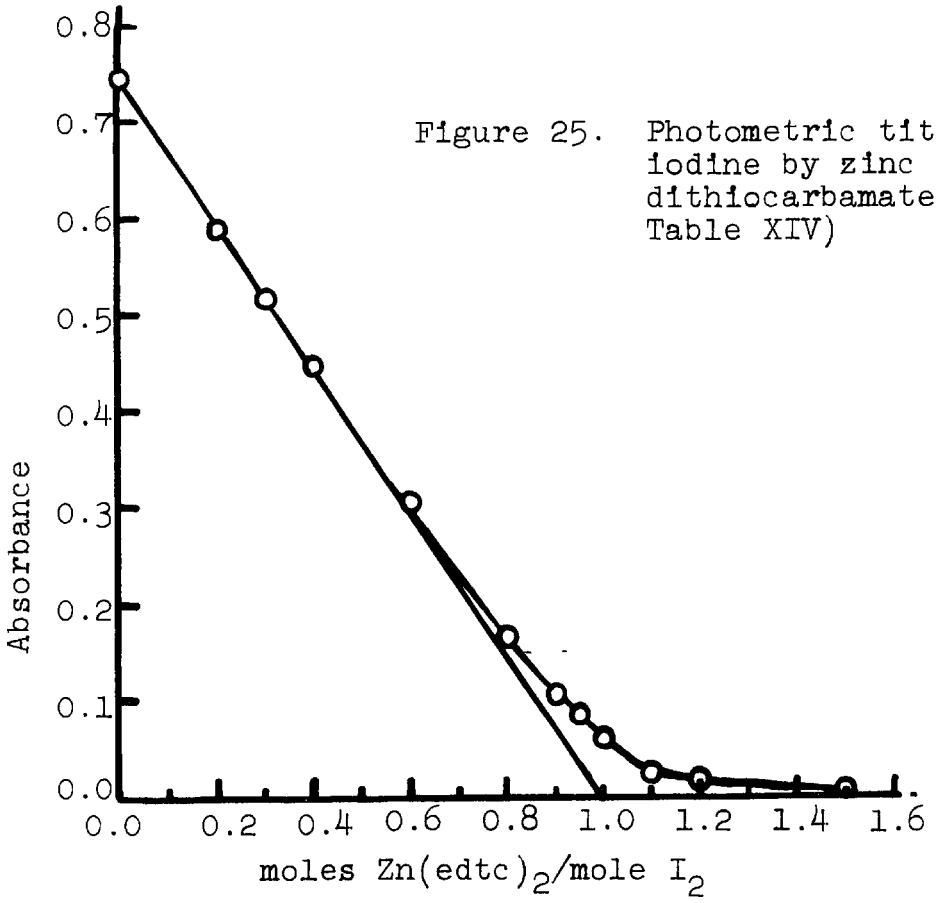


Figure 25. Photometric titration of iodine by zinc diethyldithiocarbamate (see Table XIV)

TABLE XV. Photometric titration of iodine by mercuric diethyldithiocarbamate, $Hg(edtc)_2$, in chloroform
Temp. = 22-23°C

conc. $Hg(edtc)_2$ (moles/liter)	moles $Hg(edtc)_2$ / mole I_2[a]	Absorbance[b] at 510 mμ
0.00×10^{-4}	0.000	0.742
2.51	0.301	0.517
4.18	0.502	0.373
6.68	0.802	0.146
7.52	0.901	0.076
8.35	1.00	0.008
10.4	1.25	0.000

graphical end point (see Fig. 26) = 1.00 moles Hg/mole I_2

a) conc. $I_2 = 8.35 \times 10^{-4}$M
b) path length = 1.00 cm.

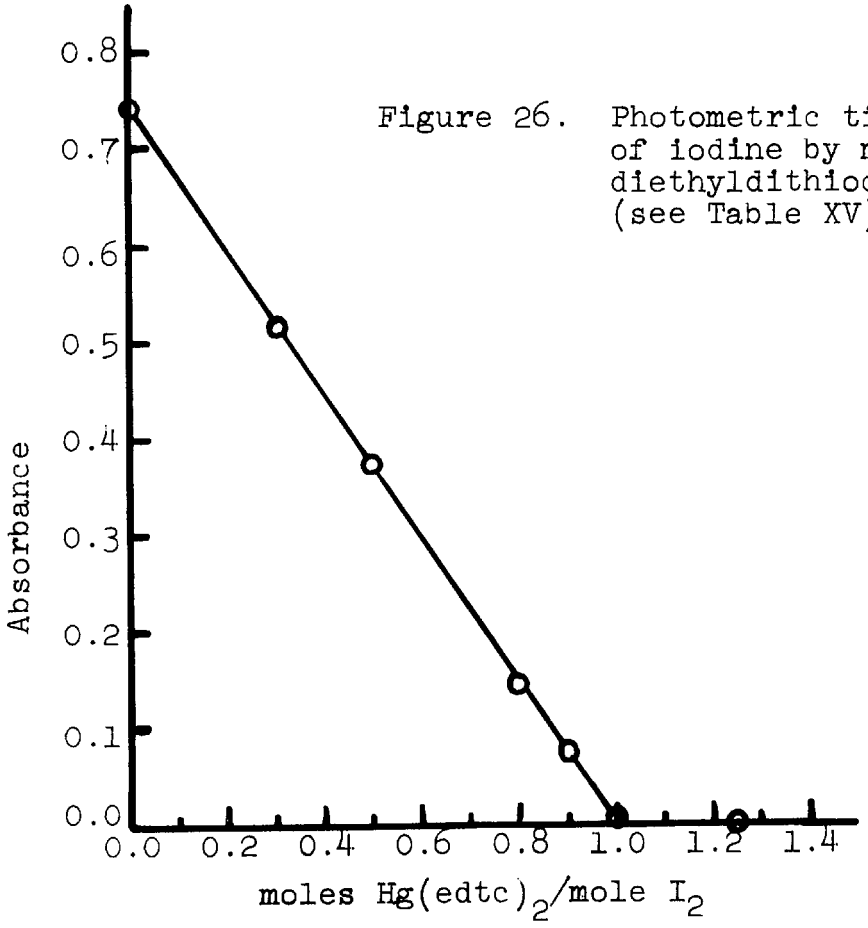


Figure 26. Photometric titration of iodine by mercuric diethyldithiocarbamate (see Table XV)

TABLE XVI. Visual titration of several metal diethyldithiocarbamates, $M(edtc)_2$, by iodine in chloroform

metal*	$M(edtc)_2$ (mmoles)	conc. I_2 (mole/l.)	ml. I_2 req'd	moles I_2 / mole $M(edtc)_2$
Hg	0.0732	5.39×10^{-3}	13.6	1.00
	0.0579	5.39	10.7	0.997
	0.102	8.97	11.15	0.980
	0.0956	8.97	10.67	1.00
Pb	0.0586	5.43	10.8	1.00
	0.0649	5.26	12.4	1.00
	0.0564	5.26	10.6	0.989
	0.0469	2.14	22.1	1.01
Cd	0.0675	5.26	12.68	0.988
	0.0602	5.26	11.25	0.983
	0.0543	2.14	25.28	0.996
Zn	0.0600	2.495	19	0.78
	0.0545	2.495	16.35	0.749
	0.0434	2.14	15.80	0.779

* All metals are in the +2 oxidation state.

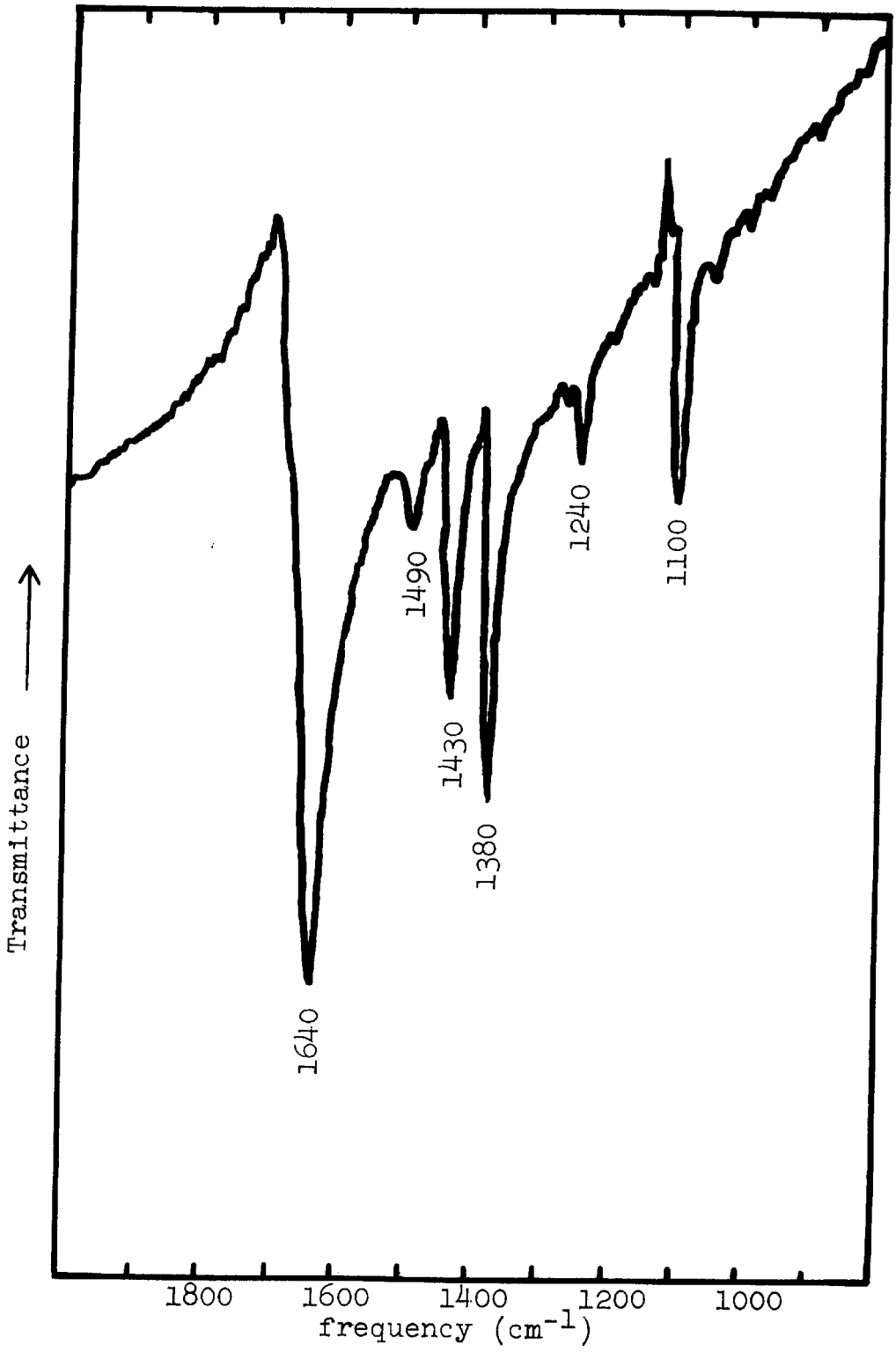


Fig. 27. Infrared spectrum of PbI_2 (recrystallized from DMF), KBr disk

to contain more than 97% of the expected yield.

The products of the reaction of $Hg(edtc)_2$ and iodine in chloroform were also identified, but no precipitation occurred for the concentration ranges employed. Thin-layer chromatography indicated that two major products were present.

A mixture of $Hg(edtc)_2$ and I_2 in chloroform was extracted with aqueous 2M potassium iodide and compared to a known sample of HgI_2 in the same medium (λ_{max} = 323 mμ, ϵ_{max} = 21,000 l./mole-cm.; this agrees with references 101 and 104). The comparison thus identified HgI_2 as one of the products, and 97.5% of the theoretical yield was accounted for.

After extracting the HgI_2, an attempt was made to isolate and purify the other product of the I_2-$Hg(edtc)_2$ reaction, but this was not successful. However, infrared spectra of the unpurified product suggested that TETD was a major component. Further support for this was obtained using an indirect analysis of TETD, suggested by Fredga (105). Solid cuprous chloride reacts with TETD in chloroform to produce cupric diethyldithiocarbamate $[Cu(edtc)_2]$ which has a very intense visible absorption maximum around 435 mμ ($\epsilon_{max} = 1.25 \times 10^4$ l./mole-cm. in chloroform). This procedure was applied to I_2-$Hg(edtc)_2$ mixtures and gave results that were comparable to those of known solutions of TETD, in approximately the yield predicted.

The ultraviolet spectra of mixtures of I_2 and $Hg(edtc)_2$

agree well with those of corresponding mixtures of HgI_2 and TETD. However, they do not match the composite spectra made up from the absorptions of isolated HgI_2 and isolated TETD. This is due to the interaction of TETD with HgI_2 to produce a new absorption band that appears as a shoulder at about 330 mμ. The interaction of these compounds was not investigated further, but the extractability of HgI_2 from solution suggests that it is easily reversible.

C. Analysis of Metal Dithiocarbamates

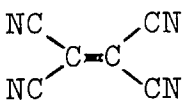
The reaction of iodine with several metal diethyldithiocarbamates may be of some analytical importance. The visual or photometric titration of these water-insoluble dithiocarbamates in an organic solvent is a rapid, simple method of analysis. This feature is lacking in the present methods of analysis of such compounds.

Currently, several analytical techniques are employed for the water-insoluble metal dithiocarbamates, as well as the water-soluble salts (106, 107). The method based on acid decomposition of these compounds (106, 108, 109, 110) is accurate, but involves subsequent analysis of one of the decomposition products. Other methods such as photometric analysis (106, 111, 112, 113), chromatography (106, 114), and polarography (115, 116) require knowledge of special physical properties of the compounds prior to analysis. The latter two methods have not been made generally useful.

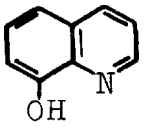
The only rapid and simple analysis of metal dithiocarbamates is the titration in aqueous solution of the water-soluble salts by mild oxidizing agents such as iodine (117). The present study now shows that this procedure can be extended very easily by using non-aqueous solvents for the water-insoluble salts.

D. Reactions of Several Metal Complexes with Some Electron Acceptors

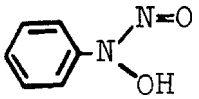
Several other metal coordination compounds were studied briefly as donors toward external acceptors. The interactions of tetracyanoethylene (TCNE, XIII) with metal oxinates (complexes with 8-hydroxyquinoline, XIV) and cupferrates (complexes with N-nitroso-N-phenylhydroxylamine, XV) in chloroform or methylene chloride were investigated



(XIII)



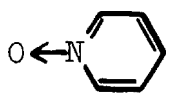
(XIV)



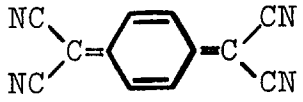
(XV)

in the ultraviolet and visible regions. Below about 320 mμ investigations were limited due to the intense absorption bands of both donor and acceptor, necessitating use of very low concentrations ($\sim 10^{-5}$M). Although TCNE does not absorb appreciably above 320 mμ, studies in this region where limited by its low solubility. Thus, for the concentrations used, there appeared to be little or no interaction in these systems.

Brief study of the cupric chloride-pyridine-N-oxide (XVI) coordination compound in acetonitrile with TCNE and tetracyanoquinodimethane (XVII) gave inconclusive results,



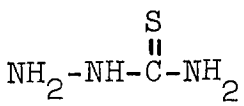
(XVI)



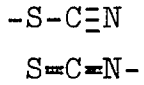
(XVII)

as before, due to the strong absorption of the compounds. Iodine was found to react too strongly with this solvent to allow its use as an acceptor in this case. "Inert" solvents could not be used because of the insolubility of the metal complex.

Thiosemicarbazide (XVIII) and thiocyanate/isothiocyanate (XIX) complexes presented a similar situation to



(XVIII)



(XIX)

the pyridine oxide case, since these complexes are generally soluble only in water. Attempts to see if iodine would coordinate led to observation of the dissociation of iodine in water, in agreement with literature results (100).

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III. INTERACTIONS OF IODINE WITH DIXANTHOGEN AND METAL XANTHATES

The interactions of iodine with diethyldixanthogen, C_2H_5O-C(S)-SS-C(S)-OC_2H_5 (commonly called dixanthogen, and abbreviated here as DIXAN), and with some metal xanthate complexes, $M^{+n}(S_2C\text{-}OC_2H_5)_n$ (abbreviated $M(exan)_n$), were explored in only a limited way. One difficulty involved the purity of dixanthogen (see Appendix). However, some data were obtained which may be suitable for qualitative comparison with the I_2-TETD and I_2-$M(edtc)_2$ systems.

A. DIXAN-I_2

Only the blue-shifted visible spectrum of the I_2-DIXAN system was investigated (Figure 28) due to the intense ultraviolet absorption of DIXAN and the high concentration of it required for appreciable interaction. Comparison of Figure 28 with that of the TETD-I_2 system (Figure 6) shows the much higher concentration of DIXAN needed, and makes it apparent that the DIXAN-I_2 complex must be considerably weaker than any of the others investigated in this work. Calculations made on the data for DIXAN-I_2 mixtures (Table XXIV, Appendix) in CCl_4 at 460 mμ (approximate maximum of the shifted iodine band) gave the following results from the modified Scott equation:

$$K_{20^\circ} = 5.3 \pm 0.7 \text{ liter/mole}; \quad \epsilon_c = 930 \text{ l./mole-cm.}$$

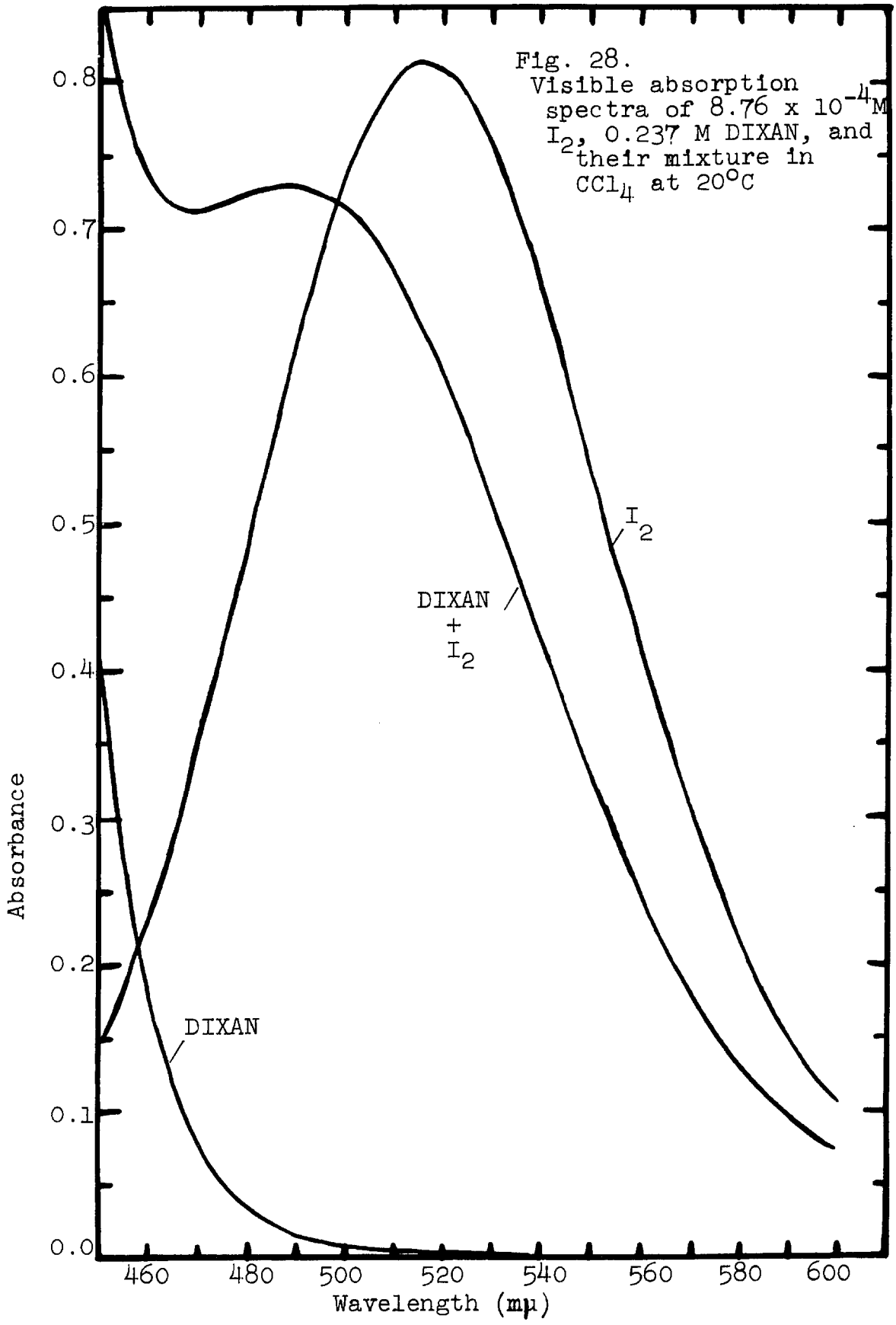


Fig. 28.
Visible absorption spectra of 8.76×10^{-4} M I_2, 0.237 M DIXAN, and their mixture in CCl_4 at 20°C

These values must be regarded as qualitative because of the unknown purity of the donor, and because of the approximations that were made for the density of the concentrated solutions. The mixtures did show an isosbestic point at about 498 mμ (indicative of only two absorbing species), and they were stable over several hours.

From the discussion of donor site presented earlier, it would be expected that DIXAN is a weaker donor toward iodine than is TETD, assuming that the thiocarbonyl sulfur is the prominant donor site in both species. However, with such a weak donor as dixanthogen, the possibility cannot be ignored that another donor site (e.g., the disulfide group) either dominates or competes with the thiocarbonyl site.

A study of the infrared spectra of dixanthogen and dixanthogen-iodine mixtures was undertaken. Dixanthogen was obtained as a yellow oil which made it easy to place between salt plates. Also, iodine is unusually soluble in dixanthogen (a 50% by weight solution of iodine was prepared), suggesting sufficient interaction to perhaps alter the infrared absorption pattern.

The infrared spectra were taken with the Perkin Elmer IR-21 and IR-337 instruments. Relatively large amounts of iodine in dixanthogen were required to produce a significant effect on the infrared absorption. For example, a 10% by weight iodine solution in the oil caused rather minor changes. A 50% by weight mixture produced large

effects, and these are listed in Table XXV (Appendix). This qualitative investigation was not pursued further because the assignments of infrared frequencies in dixanthogens have not been conclusively made (59, 62, 64, 65,66).

B. The Reaction of Metal Xanthates with Iodine

Iodine reacts with the ethylxanthate (or xanthate) complexes of zinc(II) and cadmium(II) in chloroform to produce two new absorption bands around 380 and 277 mμ. In the case of the zinc salt (absorption maximum at 299 mμ) and iodine (absorption maximum at 513 mμ), isosbestic points were located at 443, 322, and 291 mμ. These new absorption bands were not the result of complex formation since the "apparent" K (calculated from the modified Scott equation) was very large, but the temperature dependence was negligible. The ultraviolet band was near the dixanthogen absorption maximum.

Concentrated 1:1 mixtures of iodine and $Zn(exan)_2$ in chloroform or methylene chloride were evaporated under partial vacuum (heat causes a side reaction) and produced a yellow oil. This oil was identified as dixanthogen by infrared analysis.

The similarity of this reaction to that of the metal dithiocarbamates is apparent from the identification of dixanthogen in the reaction mixture. Production of a yellow oil (presumed to be dixanthogen) has been reported for the reaction of iodine with alkyl or aryl mercuric

xanthates (118). Presumably, titration of metal xanthates with iodine in organic solvents, similar to that of the metal dithiocarbamates, should be possible.

SUMMARY

A series of thiones was studied spectrophotometrically as electron donors toward iodine in carbon tetrachloride. This series included tetraethylthiuram disulfide, tetramethylthiuram disulfide, tetramethylthiuram monosulfide, methyl dimethyldithiocarbamate, and N,N-dimethylthioacetamide. Stability constants for complex formation and enthalpies and entropies of interaction were determined.

Substituent effects on the donor strength of the thioamide group, N-C=S, in this series were generally small. Comparison of the results with those on related systems from other laboratories led to the conclusion that the thiocarbonyl sulfur was the predominant donor site toward iodine. In addition, a brief study of the iodine complex with dixanthogen showed that it was much weaker than any of the other thione complexes listed above.

Iodine was found to react with several metal diethyldithiocarbamates in chloroform to produce the dimer of the ligand, tetraethylthiuram disulfide, and the metal iodide. This reaction can be followed quantitatively by visual or spectrophotometric titration, which suggests its use as a simple method for the analysis of water-insoluble metal dithiocarbamates. Similar observations, though much less extensive, were made on the I_2-metal xanthate system.

A number of other studies of interactions of electron acceptors with metal complexes were not successful.

APPENDIX I

PURIFICATION OF REAGENTS

All solid reagents, after purification, were dried under vacuum (except I_2, DMTA, and TCNE which sublime), then stored in dessicators containing calcium chloride.

CCl_4: Spectroquality carbon tetrachloride (Eastman; and Matheson Coleman and Bell) was dried over $CaCl_2$ and distilled immediately before use.

I_2: Baker "Analyzed" Reagent Iodine was resublimed from a pulverized mixture of iodine and potassium iodide. The resublimed product was stored in a dessicator in the dark.

TETD: Tetraethylthiuram disulfide was obtained from Matheson Coleman and Bell, and was recrystallized twice from ethanol. m.p. 70-71°C; literature: 70.5°C (119), 72°C (106).

TMTD: Tetramethylthiuram disulfide was obtained from Matheson Coleman and Bell and was recrystallized twice from chloroform-ethanol. m.p. 154-156°C; literature: 151°C (119), 156°C (106).

TMTM: Tetramethylthiuram monosulfide was obtained from Eastman Organic Chemicals, and was recrystallized twice from ethanol. m.p. 105-106°C; literature: 104°C (119), 106°C (106).

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MMDTC: Methyl dimethyldithiocarbamate was prepared from dimethylammonium dimethyldithiocarbamate (Eastman) and methyl iodide in aqueous solution in 1:1 mole ratio. The mixture was stirred for about 1 hour at 30-40°C. After cooling, the solution was extracted several times with ethyl ether, then recrystallized twice from 40-60°C petroleum ether. m.p. 46-47°C; literature values: 45-46°C (120), 47°C (106). Analysis - Calculated for $C_4H_9NS_2$: 35.52% C, 6.71% H, 47.42% S; found: 35.60% C, 6.60 % H, 47.50% S.

DMTA: N,N-dimethylthioacetamide was obtained from Eastman Organic Chemicals, and was recrystallized twice from water. Since melting point data were not available, an analysis was obtained. Calculated for C_4H_9NS: 46.55% C, 8.79% H, 31.07% S; found: 46.59% C, 8.74% H, 31.10% S.

THIA: Thioacetamide was obtained from Eastman Organic Chemicals and was recrystallized from anhydrous ethyl ether. Its ultraviolet spectrum agreed with the literature (17).

$Hg(edtc)_2$: Mercury(II) diethyldithiocarbamate was prepared by mixing aqueous solutions of sodium diethyldithiocarbamate (Eastman) and either mercuric nitrate or acetate. The yellow precipitate was recrystallized twice from chloroform-ethanol. m.p. 140-141°C. Analysis - Calculated for $C_{10}H_{20}N_2S_4Hg$: 24.16% C, 4.05% H, 25.80% S; found: 24.29% C, 4.17% H, 25.76% S. Several attempts to prepare this product by adding solid sodium diethyldithiocarbamate to mercuric nitrate solutions produced a

yellow-white precipitate that was mostly insoluble in chloroform. Attempts to purify the chloroform-soluble portion of the mixture were not successful.

$Pb(edtc)_2$: Lead(II) diethyldithiocarbamate was prepared by mixing aqueous solutions of sodium diethyldithiocarbamate and lead nitrate. The cream-colored precipitate was recrystallized with difficulty from chloroform-ethanol, and more easily from carbon tetrachloride. Analysis - Calculated for $C_{10}H_{20}N_2S_4Pb$: 23.84% C, 4.00% H, 25.46% S; found: 23.56% C, 3.60% H, 25.19% S.

$Cd(edtc)_2$: Cadmium(II) diethyldithiocarbamate was prepared by mixing aqueous solutions of sodium diethyldithiocarbamate and cadmium chloride. The white precipitate was recrystallized from methylene chloride-ethanol. Analysis - Calculated for $C_{10}H_{20}N_2S_4Cd$: 29.37% C, 4.93% H, 31.36% S; found: 29.33% C, 4.84% H, 31.39% S.

$Zn(edtc)_2$: Zinc(II) diethyldithiocarbamate was prepared by mixing aqueous solutions of sodium diethyldithiocarbamate and zinc nitrate. The white precipitate was recrystallized from chloroform or chloroform-ethanol. Analysis - Calculated for $C_{10}H_{20}N_2S_4Zn$: 33.19% C, 5.57% H, 35.44% S; found: 33.35% C, 5.46% H, 35.50 % S.

$Zn(exan)_2$: Zinc(II) ethylxanthate was prepared by mixing aqueous solutions of potassium ethylxanthate and zinc nitrate. The white precipitate was recrystallized from chloroform. Its infrared spectrum checked with that in the literature (65).

TCNE: Tetracyanoethylene was obtained from K and K Laboratories, Inc. This was recrystallized from chlorobenzene, filtered, and washed with chloroform. The product was then sublimed in a closed system under dry nitrogen atmosphere from an oil bath maintained at 110-130°C. The final product was pure white and crystalline. m.p. (sealed tube) 195-196°C; literature: 198-200°C (124), 197-198°C (125).

Purification of Dixanthogen: Dixanthogen was prepared by the oxidation of potassium ethylxanthate (Eastman Organic Chemicals) with either iodine or potassium persulfate in aqueous solution. A yellow oil formed which was extracted by ether, dried over sodium or magnesium sulfate, and recovered by evaporation of the ether. The oil was then distilled under vacuum at about 100°C. Three samples were analyzed for sulfur content (52.91% S calculated for $C_6H_{10}O_2S_4$). For the undistilled oil, 54.80% S was found; for the same oil after distillation, 52.85% S was found; and for a different batch of oil after distilling, 55.00% S was found. These analyses suggest that distillation may be an adequate purification technique, but that it may not always be effective.

The infrared spectrum of the oil was identical to published data (62, 65, 66, 121), but the physical state contrasted with reports (122, 123) that dixanthogen (recrystallized from alcohol) was a colorless, crystalline solid melting at about 32°C. One of these studies reported

a carbon, hydrogen, sulfur analysis which agreed with calculated values.

A very small amount of oil was dissolved in warm ethanol and was crystallized in a dry ice-acetone bath (about -78°C). However, the white precipitate first obtained became a yellow oil on standing in air overnight (room temperature about 20-25°C). The original oil can be frozen in a dry ice-acetone bath to a yellow-white solid which melts much below room temperature.

Purification of Carbon Tetrachloride: The extinction coefficient and band position of iodine are susceptible to differences in solvents, and are especially susceptible to small quantities of certain impurities (such as amines and sulfides) in an "inert" solvent. Thus it seemed reasonable to use as a measure of solvent purity the visible absorption band of iodine.

Five purification procedures were used to determine the quality of CCl_4 most suitable for this work. The procedures are as follows:

(1) dry: Analytical Reagent Grade was dried over $CaCl_2$, and distilled.

(2) KOH-dry: Analytical Reagent Grade was washed several times with KOH solution, then water, then dried over $CaCl_2$, and distilled.

(3) Spectro: Spectroquality solvent was used with no further purification.

(4) Spectro-dry: Spectroquality was dried over $CaCl_2$,

and distilled.

(5) Pure: Analytical Reagent Grade was refluxed over mercury, washed in sequence with concentrated H_2SO_4, KOH, and H_2O, then dried over $CaCl_2$ and distilled (126).

Results:

	# trials	$\lambda_{max} = 516 \pm 1$ mμ ϵ_{max} (l./mole-cm.)
(1) dry	7	919 ± 6
(2) KOH-dry	7	920 ± 7
(3) Spectro	2	907 ± 2
(4) Spectro-dry	8	924 ± 6
(5) Pure	2	934 ± 1

It seems reasonable to assume that impurities (unless they absorb in the visible region) would tend to reduce the absorption band intensity of iodine. If this is the case, the "pure" CCl_4 appears to be the best solvent. However, the involved technique required for purification and the large volume of solvent consumed per spectrophotometric run (ca. 500 ml.) made it more practical to use the "Spectro-dry" procedure.

APPENDIX II

DATA TABLES

The abbreviations used in the following tables are:

I_o - initial concentration of iodine

D_o - initial concentration of donor

A - absorbance of mixture, corrected for absorbance of donor and iodine

A_{norm} - absorbance normalized for the given wavelength according to the Liptay procedure (see section on Calculations)

b - path length

ϵ - molar extinction coefficient at the given wavelength

TABLE XVII. Data for TETD-I_2 at 356 mμ

ϵ_{I_2} = 11 l./mole-cm. ϵ_{TETD} = 190 l./mole-cm. b = 1.00 cm.

$I_o \times 10^3$ (mole/l.)	$D_o \times 10^5$ (mole/l.)	A^*_{norm}	$(D_o+I_o) \times 10^4$ (mole/liter)	$D_oI_ob/A \times 10^8$ (mole^{2}cm./liter^2)
T = 10.0° C				
4.39	2.56	0.552	44.2	20.4
3.29	3.19	0.576	33.1	18.2
3.21	5.39	0.974	32.6	17.8
5.61	3.16	0.779	56.4	22.7
3.04	4.15	0.768	30.8	16.4
2.92	2.84	0.484	29.4	17.1
5.22	2.35	0.569	52.5	21.5
4.24	3.21	0.671	42.7	20.3
4.10	3.24	0.671	41.3	19.8
5.58	1.49	0.335	55.9	24.8
T = 15.4° C				
4.58	2.39	0.462	46.0	23.7
3.66	3.36	0.575	36.9	21.4
3.66	2.39	0.411	36.9	21.3
2.29	3.36	0.442	23.3	17.5
T = 20.0° C				
3.00	4.10	0.595	30.4	20.7
2.88	2.81	0.385	29.1	21.0
5.16	2.32	0.458	51.8	26.1
4.19	3.17	0.538	42.2	24.7
4.05	3.20	0.510	40.8	25.4
5.51	1.47	0.278	55.2	29.2
4.34	2.53	0.434	43.7	25.3
3.24	3.15	0.434	32.7	23.5
3.17	5.33	0.745	32.2	22.7
5.54	3.12	0.619	55.7	27.9
4.55	2.38	0.407	45.7	26.6
3.64	2.38	0.365	36.6	23.7
3.64	3.34	0.504	36.7	24.1
2.28	3.34	0.380	23.1	20.0
T = 25.0° C				
4.52	2.37	0.359	45.5	29.8
3.62	2.37	0.319	36.4	26.8
3.62	3.32	0.444	36.5	27.1
2.27	3.32	0.323	23.0	23.3

(Table cont'd on next page)

* From measurements at 340, 350, 356, 360, 370, 380, 390 mμ.

Table XVII (cont'd)

$I_o \times 10^3$	$D_o \times 10^5$	A_{norm}	$(D_o+I_o) \times 10^4$	$D_oI_ob/A \times 10^8$
T = 30.0° C				
4.29	2.50	0.348	43.1	30.7
3.20	3.11	0.341	32.3	29.2
3.13	5.27	0.574	31.8	28.7
5.47	3.08	0.505	55.0	33.4
2.96	4.05	0.441	30.0	27.2
2.85	2.78	0.294	28.7	26.9
5.10	2.29	0.362	51.2	32.3
4.14	3.13	0.424	41.7	30.5
4.00	3.16	0.404	40.3	31.3
5.44	1.45	0.222	54.6	35.6

TABLE XVIII. Data for TETD-I_2 at 460 mμ

ϵ_{I_2} = 264 l./mole-cm. ϵ_{TETD} negligable b = 1.00 cm.

$I_o \times 10^4$ (mole/l.)	$D_o \times 10^3$ (mole/l.)	A	$(D_o+I_o) \times 10^4$ (mole/liter)	$D_o I_o b/A \times 10^7$ (mole^{2}cm./liter^2)
T = 10.0° C				
3.83	7.30	0.810	76.8	34.5
3.84	5.48	0.747	58.6	28.1
3.84	2.93	0.580	33.1	19.3
3.84	1.46	0.392	18.4	14.3
3.85	0.732	0.240	11.2	11.7
T = 20.0° C				
3.78	7.21	0.697	75.9	39.1
3.79	5.41	0.618	57.9	33.2
3.79	2.89	0.453	32.7	24.2
3.79	1.44	0.289	18.2	18.9
3.80	0.723	0.166	11.0	16.6
T = 30.0° C				
3.73	7.12	0.575	75.0	46.2
3.74	5.34	0.503	57.2	39.8
3.74	2.86	0.352	32.3	30.4
3.74	1.42	0.210	18.0	25.4
3.75	0.714	0.118	10.9	22.7

TABLE XIX. Data for TMTD-I_2 at 354 mμ

ϵ_{I_2} = 11 l./mole-cm. ϵ_{TMTD} = 190 l./mole-cm. b = 1.00 cm.

$I_o \times 10^3$ (mole/l.)	$D_o \times 10^5$ (mole/l.)	A^*_{norm}	$(D_o+I_o) \times 10^4$ (mole/liter)	$D_o I_o b/A \times 10^8$ (mole^{2}cm./liter^2)
T = 10.0° C				
1.62	11.9	1.133	17.4	17.1
1.68	13.4	1.274	18.1	17.6
2.35	6.69	0.806	24.1	19.5
1.68	9.36	0.883	17.7	17.8
1.35	9.36	0.740	14.4	17.0
1.68	6.69	0.640	17.5	17.6
3.36	6.69	0.986	34.3	22.8
T = 15.4° C				
2.25	7.11	0.705	23.2	22.7
3.21	4.75	0.587	32.6	25.9
1.61	11.9	0.939	17.3	20.4
2.33	6.65	0.663	24.0	23.4
1.67	9.31	0.724	17.6	21.5
1.34	9.31	0.601	14.3	20.7
T = 20.0° C				
2.24	7.07	0.591	23.1	26.8
3.19	4.72	0.503	32.4	29.9
1.60	11.8	0.758	17.2	24.9
2.56	9.43	0.870	26.5	27.7
3.83	7.07	0.862	39.0	31.4
1.66	13.2	0.887	17.9	24.7
2.65	9.25	0.912	27.4	26.9
2.32	6.61	0.570	23.9	26.9
1.66	9.25	0.611	17.5	25.1
1.33	9.25	0.508	14.2	24.2
T = 30.0° C				
2.21	6.98	0.437	22.8	35.4
3.15	4.66	0.382	32.0	38.4
1.58	11.7	0.554	17.0	33.2
2.53	9.32	0.628	26.2	37.5
1.64	13.0	0.614	17.7	34.8
2.62	9.14	0.646	27.1	37.0

* From measurements at 340, 350, 354, 360, 370, 380, 390 mμ.

TABLE XX. Data for TMTM-I_2 at 330 mμ

ϵ_{I_2}=16.5 l./mole-cm. ϵ_{TMTM} = 2610 l./mole-cm. b = 1.00 cm.

$I_o \times 10^4$ (mole/l.)	$D_o \times 10^5$ (mole/l.)	A^*_{norm}	$(D_o+I_o) \times 10^4$ (mole/liter)	$D_o I_o b/A \times 10^8$ (mole^{2}cm./liter^2)
T = 10.0° C				
6.52	5.40	0.394	7.06	8.93
3.26	5.40	0.223	3.80	7.88
9.80	9.00	0.840	10.7	10.5
13.1	5.40	0.602	13.6	11.8
7.82	3.60	0.296	8.18	9.52
T = 15.2° C				
6.48	5.37	0.329	7.02	10.6
9.74	8.95	0.742	10.6	11.7
13.0	5.37	0.536	13.6	13.0
8.12	4.47	0.335	8.57	10.8
3.24	8.95	0.299	4.14	9.68
T = 20.0° C				
3.52	12.7	0.377	4.79	11.9
7.04	12.7	0.684	8.31	13.1
7.04	5.06	0.276	7.55	12.9
10.6	5.06	0.375	11.1	14.3
3.52	25.3	0.761	6.05	11.7
T = 30.0° C				
3.22	14.9	0.273	4.71	17.6
6.44	14.9	0.510	7.93	18.8
6.44	5.98	0.194	7.04	19.8
9.68	5.98	0.288	10.3	20.1
5.15	8.96	0.254	6.05	18.2

* From measurements at 310, 320, 330, 340, 350, 360 mμ.

TABLE XXI. Data for MMDTC-I_2 at 347 mμ

ϵ_{I_2} = 13 l./mole-cm. ϵ_{MMDTC} = 82 l./mole-cm. b = 1.00 cm.

$I_o \times 10^3$ (mole/l.)	$D_o \times 10^4$ (mole/l.)	A^*_{norm}	$(D_o+I_o) \times 10^4$ (mole/liter)	$D_o I_o b/A \times 10^8$ (mole^{2}cm./liter^2)
T = 10.0° C				
1.39	0.826	0.733	14.7	15.6
0.557	2.07	0.863	7.63	13.3
0.557	4.13	1.615	9.70	14.2
1.11	1.65	1.228	12.8	15.0
0.557	2.90	1.156	8.46	13.9
T = 15.4° C				
0.693	2.14	0.859	9.07	17.3
1.73	0.858	0.733	18.2	20.3
1.39	1.72	1.217	15.6	19.6
1.04	1.72	0.970	12.1	18.4
1.04	3.00	1.678	13.4	18.5
T = 20.0° C				
1.37	0.816	0.481	14.5	23.3
0.550	2.04	0.548	7.54	20.5
0.550	4.08	1.042	9.58	21.5
1.10	1.63	0.806	12.6	22.2
0.550	2.86	0.745	8.36	21.1
0.689	2.13	0.709	9.02	20.7
1.72	0.853	0.613	18.1	23.9
1.38	1.71	1.014	15.5	23.3
1.03	1.71	0.809	12.0	21.8
1.03	2.98	1.381	13.3	22.2
T = 30.0° C				
0.681	2.10	0.464	8.91	30.9
1.70	0.843	0.415	17.8	34.5
1.36	1.69	0.682	15.3	33.8
1.02	1.69	0.531	11.9	32.4
1.02	2.94	0.922	13.1	32.5

* From measurements at 330, 340, 347, 350, 360, 370, 380 mμ.

TABLE XXII. Data for DMTA-I_2 at 310 mμ

ϵ_{I_2} = 22 l./mole-cm. ϵ_{DMTA} = 253 l./mole-cm. b = 1.00 cm.

$I_o \times 10^4$ (mole/l.)	$D_o \times 10^5$ (mole/l.)	A^*_{norm}	$(D_o+I_o) \times 10^4$ (mole/liter)	$D_o I_o b/A \times 10^9$ (mole^{2}cm./liter^2)
T = 5.0° C				
1.18	8.72	0.947	2.05	10.9
2.36	5.80	1.033	2.94	13.3
4.71	5.80	1.421	5.29	19.3
0.406	9.49	0.424	1.36	9.08
1.02	9.49	0.937	1.96	10.3
1.43	9.49	1.167	2.37	11.6
2.04	6.33	1.051	2.67	12.3
T = 10.0° C				
1.46	6.78	0.758	2.14	13.0
0.582	17.0	0.699	2.28	14.2
2.92	6.78	1.192	3.59	16.6
8.73	2.03	0.564	8.94	31.5
1.17	8.66	0.781	2.04	13.0
2.35	5.77	0.939	2.92	14.4
4.69	5.77	1.264	5.26	21.4
0.404	9.43	0.351	1.35	10.8
1.01	9.43	0.782	1.95	12.2
1.42	9.43	1.009	2.36	13.2
2.02	6.30	0.900	2.65	14.2
T = 20.0° C				
1.44	6.70	0.500	2.11	19.3
0.575	16.8	0.472	2.26	20.5
2.88	6.70	0.837	3.55	23.1
8.63	2.01	0.455	8.83	38.1
1.16	8.56	0.518	2.02	19.2
1.16	14.3	0.805	2.59	20.6
2.32	5.70	0.627	2.89	21.1
2.32	14.3	1.416	3.75	23.2
4.63	5.70	0.974	5.20	27.1
0.399	9.32	0.215	1.33	17.3
0.998	9.32	0.501	1.93	18.6
1.40	9.32	0.664	2.33	19.7
2.00	6.22	0.608	2.62	20.5

(Continued on next page.)

* From measurements at 300, 310, 320, 330, 340, 350, 360 mμ.

(TABLE XXII continued)

$I_o \times 10^4$	$D_o \times 10^5$	A^*_{norm}	$(D_o+I_o) \times 10^4$	$D_o I_o b/A \times 10^9$
T = 30.0° C				
1.15	8.46	0.324	1.99	29.9
1.15	14.1	0.512	2.56	31.6
2.29	5.63	0.401	2.85	32.2
2.29	14.1	0.939	3.70	34.5
4.57	5.63	0.671	5.14	38.4

TABLE XXIII. Data for DMTA-I_2 at 340 mμ

ϵ_{I_2} = 14 l./mole-cm. ϵ_{DMTA} = 48 l./mole-cm. b = 1.00 cm.

$I_o \times 10^4$ (mole/l.)	$D_o \times 10^5$ (mole/l.)	A^*_{norm}	$(D_o+I_o) \times 10^4$ (mole/liter)	$D_o I_o b/A \times 10^9$ (mole^{2}cm./liter^2)
T = 5.0° C				
1.18	8.72	0.557	2.05	18.5
2.36	5.80	0.608	2.94	22.6
4.71	5.80	0.835	5.29	32.7
0.406	9.49	0.248	1.36	15.5
1.02	9.49	0.550	1.96	17.5
1.43	9.49	0.684	2.37	19.8
2.04	6.33	0.618	2.67	20.9
T = 10.0° C				
1.46	6.78	0.450	2.14	21.9
0.582	17.0	0.415	2.28	23.8
2.92	6.78	0.711	3.59	27.8
8.73	2.03	0.334	8.94	53.2
1.17	8.66	0.463	2.04	22.0
2.35	5.77	0.528	2.92	25.7
0.404	9.43	0.209	1.35	18.2
1.01	9.43	0.444	1.95	21.4
1.42	9.43	0.598	2.36	22.3
2.02	6.30	0.534	2.65	23.9
4.69	5.77	0.751	5.26	36.0
T = 20.0° C				
1.44	6.70	0.300	2.11	32.1
0.575	16.8	0.282	2.26	34.2
2.88	6.70	0.509	3.55	37.9
8.63	2.01	0.275	8.83	63.1
1.16	8.56	0.315	2.02	31.5
1.16	14.3	0.490	2.59	33.9
2.32	5.70	0.378	2.89	35.0
2.32	14.3	0.861	3.75	38.5
4.63	5.70	0.592	5.20	44.6
0.399	9.32	0.128	1.33	29.1
0.998	9.32	0.301	1.93	30.9
1.40	9.32	0.401	2.33	32.6
2.00	6.22	0.365	2.62	34.1

(continued on next page)

* From measurements at 300, 310, 320, 330, 340, 350, 360 mμ.

(Table XXIII continued)

$I_o \times 10^4$	$D_o \times 10^5$	A_{norm}	$(D_o+I_o) \times 10^4$	$D_oI_ob/A \times 10^9$
T = 30.0° C				
1.15	8.46	0.203	1.99	47.8
1.15	14.1	0.318	2.56	51.0
2.29	5.63	0.248	2.85	52.0
2.29	14.1	0.582	3.70	55.6
4.57	5.63	0.416	5.14	61.9

TABLE XXIV. Data for DIXAN-I_2 at 460 mμ

ϵ_{I_2} = 264 l./mole-cm. ϵ_{DIXAN} = 0.764 l./mole-cm.

Temp. = 20.0°C b = 1.00 cm.

$I_o \times 10^4$ (liter/mole)	D_o[a] (liter/mole)	A_{uncorr}	A_{corr}[b]
8.76	0.237	0.734	0.321
8.76	0.159	0.621	0.268
8.76	0.119	0.554	0.232
8.76	0.0790	0.460	0.168
8.76	0.0395	0.361	0.100

a) The molar concentration of dixanthogen was approximated by using a density of 1.27 g./ml. at 20°C which was based on a density given for 25°C (127).

b) Absorbance corrected for initial concentrations of donor and iodine.

TABLE XXV. Infrared frequencies (1300-400 cm^{-1}) for DIXAN and DIXAN + I_2

w - weak m - medium s - strong sh - shoulder

DIXAN		DIXAN + 50% I_2	
1290	(sh)	1270	(m)
1270	(s)	1260	
1240		1205	(s)
1150	(m)	1140	(w)
1110	(ms)		
1090	(sh)		
1040	(s)	1050	(w)
1020		970	(mw)
1000	(sh)	950	(mw)
850	(m)	870	(s)
810	(w)		
790	(m)	790	(mw)
760	(w)	760	(m)
no distinct absorption below 700, but several very weak, irregular absorptions		500	(mw)

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