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A Study of the Spectroscopic, Thermodynamic, and Dielectric Properties of the t-Butylbenzene/Tetracyanoethylene Molecular Complex

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A Study of the Spectroscopic, Thermodynamic, and Dielectric Properties of the t-Butylbenzene /Tetracyanoethylene Molecular Complex

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BY

Donald W. Mundell

THESIS

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CHARLESTON, ILLINOIS

1976
YEAR

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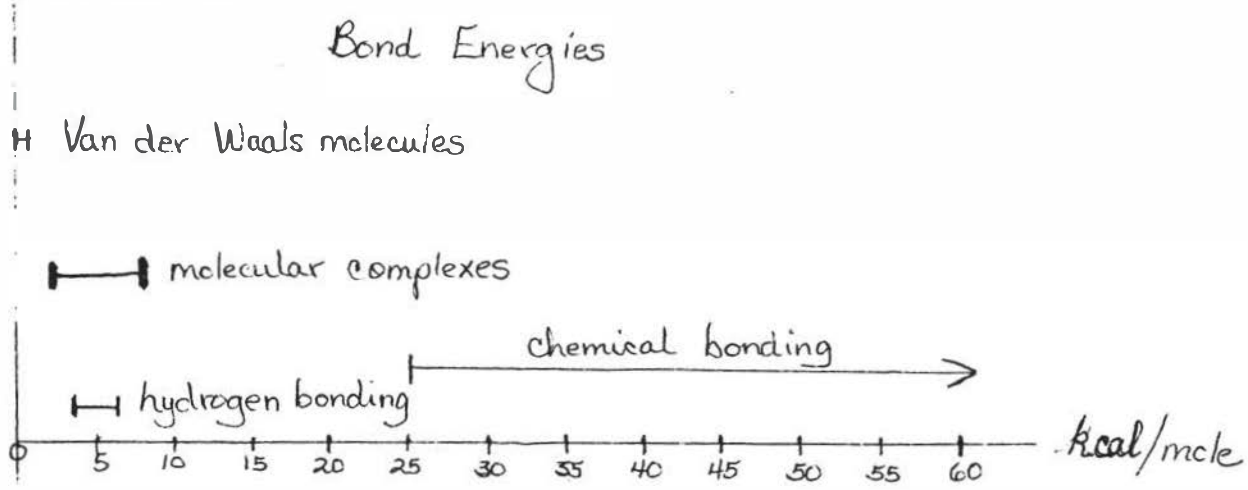
INTRODUCTION

A molecular complex is defined as "an association between two molecules, somewhat stronger than ordinary Van der Waals associations, of definite stoichiometry"(1). Evidence for complex formation can be found in the uv-visible spectrum which exhibits, on mixing of the two components, a new band unique to the complex (2). Complexes of aromatic compounds with tetracyanoethylene (TCNE) are typically highly colored; benezene gives a yellow solution, t-butylbenzene(TBB) an orange, durene a red, and hexamethylbenzene a deep purple.

The theory which best describes the properties of molecular complexes is the charge transfer reasonance theory developed by Mulliken (1). The bonding properties of these complexes are intermediate between those of weakly bound Van der Waals complexes and ionic bonding:



The ground (ψ_N) and excited (ψ_E) state wavefunctions are therefore considered to be a linear combination of wavefunctions describing a "no bond" and a dative form.

$$\psi_N(DA) = a\,\psi_0(D,A) + b\,\psi_1(A^- - D^+)$$
$$\psi_E(DA) = b^*\,\psi_0(D,A) + a^*\,\psi_1(A^- - D^+)$$

The wavefunction ψ_0 is called the "no bond" function. It represents binding due to forces such as dipole-dipole, dipole-induced dipole, London dispersion forces, and hydrogen bonding. The wavefunction ψ_1 is called the dative function. It corresponds to a structure where one electron has been completely transfered from donor to acceptor. The transfer is usually considered to occur from the highest filled orbital of the donor to the lowest unoccupied orbital of the acceptor. Normalizing the wavefunctions leads to the following equations.

$$\int \psi_N \psi_N \, d\tau = a^2 + b^2 + 2ab S_{01}$$
$$\int \psi_E \psi_E \, d\tau = a^{*2} + b^{*2} + 2ab S_{01}$$

where it is assumed that the eigenvectors (a,b,a*,b*) are independent of spatial coordinates, S_{01} refers to $\int \psi_1 \psi_0 \, d\tau$, and $\int \psi_1 \psi_1 \, d\tau$, $\int \psi_0 \psi_0 \, d\tau$ are equal to one. In general the ground state is considered to have less dative character than the excited state; thus transitions from ground to excited states are termed charge transfer transitions. The energy of the ground state of the complex (W_n) is obtained by operating with the Hamiltonian on the weighted approximate wavefunctions ψ_0 and ψ_1 according to the quantum mechanical averaging process for nonexact functions:

$$W_N = \frac{\int \psi_N^* \hat{H} \psi_N \, d\tau}{\int \psi_N \psi_N \, d\tau} = \frac{\int (a\psi_0 + b\psi_1)^* \hat{H} (a\psi_0 + b\psi_1)}{a^2 + b^2 + 2ab S_{01}}$$
$$= (a^2 W_0 + b^2 W_1 + 2ab H_{01}) / (a^2 + b^2 + 2ab S_{01})$$

where W_0, W_1 are equal to $\int \psi_0 \hat{H} \psi_0 \, d\tau$, $\int \psi_1 \hat{H} \psi_1 \, d\tau$, and H_{01} is equal to $\int \psi_0 \hat{H} \psi_1 \, d\tau = \int \psi_1 \hat{H} \psi_0 \, d\tau$ (assuming $\hat{H}$ is a hermitian operator for ψ_1, ψ_0).

The corresponding equation for the excited state is:

$$W_E = (a^{*2} W_0 + b^{*} W_1 + 2a^{*} b^{*} H_{01}) / (a^{*2} + b^{*2} + 2a^{*} b^{*} S_{01})$$

If according to variational theory the energy is minimized with respect to a and b to give the lowest energy wavefunction:

$$\frac{dW_N}{da} = 0 = \frac{dW_N}{db}$$

The following equations are obtained.

$$(I)\quad a(W_0 - W_N) + b(H_{01} - S_{01}W_N) = 0$$

$$(II)\quad a(H_{01} - S_{01}W_N) + b(W_1 - W_N) = 0$$

or

$$\begin{vmatrix} W_0 - W_n & H_{01} - S_{01}W_n \\ H_{01} - S_{01}W_n & W_1 - W_n \end{vmatrix} \cdot \begin{vmatrix} a \\ b \end{vmatrix} = 0$$

Setting the determinate of the energy matrix equal to zero:

$$(W_0 - W_n)(W_1 - W_n) - (H_{01} - S_{01}W_n)^2 = 0$$

Rearranging:

$$(III)\quad (W_0 - W_n)(W_1 - W_n) = (H_{01} - S_{01}W_n)^2$$

$$\therefore\ (IV)\quad W_n = W_0 - \frac{B_n^2}{W_1 - W_n}$$

Where B_n is equal to $H_{01}-S_{01}W_n$. A similar treatment of the excited state yields:

$$(V)\quad W_e = W_1 - \frac{B_e^2}{W_0 - W_e}$$

Where B_e refers to $H_{01}-S_{01}W_e$. The transition energy (hv) between ground and excited states is given by the difference between equations (IV) and (V).

$$(VI)\quad h\nu = W_e - W_n = W_1 - W_0 + \frac{B_n^2}{W_1 - W_n} - \frac{B_e^2}{W_0 - W_e}$$

For weak complexes the dative form contributes much less than the "no bond" structure ($b << a$); therefore W_n and W_e may be approximated by W_0 and W_1 since they differ by the resonance energy between the dative and "no bond" structure. Therefore equation (VI) becomes:

$$(VII)\quad h\nu = W_1 - W_0 + \frac{C_2}{W_1 - W_0}$$

Where C_2 refers to $B_n^2 + B_e^2$. The quantum energies in the above equation can be related to experimentally determined ionization potentials and electron affinities by considering the following process (3).

1. $D \rightarrow D^{+}+e^{-}$ $\Delta E1 = I_D^V$, the vertical ionization potential of the donor (D)

2. $e^{-} + A \longrightarrow A^{-}$ $\Delta E_2 = {}^{-}E_A^V$, the electron affinity of the acceptor (A)

3. $(A^{-} + D^{+})_{\infty} \longrightarrow A^{-} \cdots D^{+}$ $\Delta E_3 = G_1$ the columbic energy of bringing the two charges together

The total process leads to W_1, the energy of the dative state from $(D + A)_{\infty}$ or W_0 (if we assume the Van der Waals stabilization is small) ∴ (VIII) $W_1 - W_0 = I_D^V - E_A^V - G_1$

Where G_1 is $e^2/r + X$ and X is the polarization of the charge transfer bond at the dative state. Figure 1 provides an energy level diagram relating the energies discussed above. Substituting equation (VIII) into equation (VII):

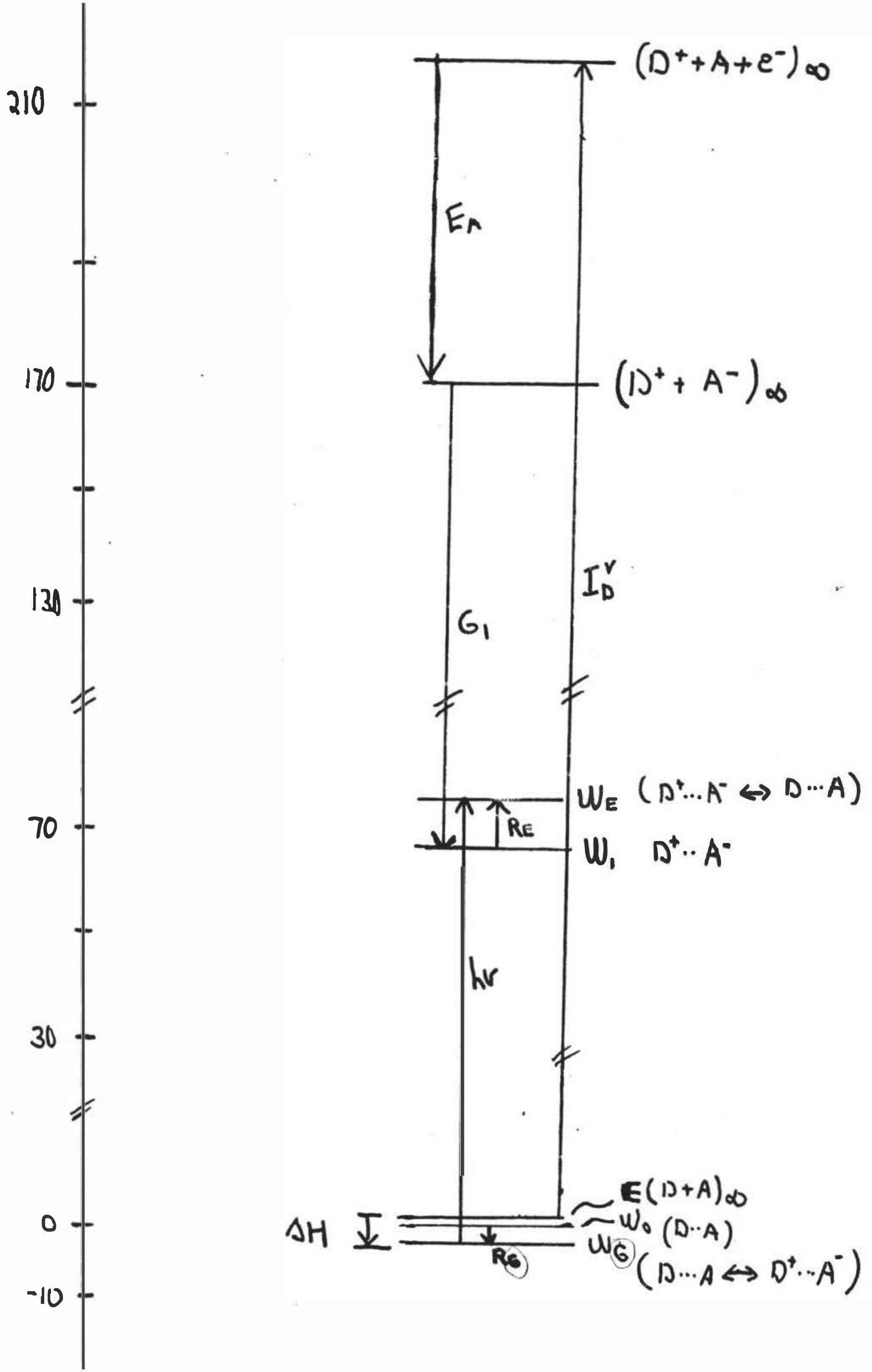
$$(IX) \quad h\nu_{ct} = I_D^V - E_A^V - G_1 \frac{B_n^2 + B_e^2}{I_D^V - E_A^V - G_1}$$

For a series of similar complexes with the same acceptor, E_A is rigorously constant. If the intermolecular separation remains constant, G_1, S_{01}, H_{01}, W_n, W_e and therefore B_n and B_e will be approximately constant, since similar π orbitals are involved in the overlap. Since I_D^V can be made to vary over a small range, a nearly linear plot of hv versus I_D^V for such a series might be expected. Chan and Liao (4) have found this to be the case for a series of methylated benzenes complexed with TCNE and have evaluated G_1 and $C_2 \equiv B_n^2 + B_e^2$ by two independent means (Spectroscopic and dipole measurements) with good agreement.

Assuming W_0 is very nearly zero, equation (IV) can be equated to ΔH (see Fig. 1).

Figure 1

Energy level diagram for molecular complex of tetracyanoethylene with benzene(4)


$(D^{+}+A+e^{-})_{\infty}$
210
E_A
170
$(D^{+}+A^{-})_{\infty}$
130
G_1
I_D^{v}
W_E $(D^{+}\cdots A^{-} \leftrightarrow D\cdots A)$
70
R_E
W_1 $D^{+}\cdot\cdot A^{-}$
$h\nu$
30
$E(D+A)_{\infty}$
0
W_0 $(D\cdot\cdot A)$
ΔH
R_G
W_G $(D\cdots A \leftrightarrow D^{+}\cdot\cdot A^{-})$
-10

(X) $$\Delta H^\circ = W_0 - \frac{B_n^2}{W_1 - W_0} = W_0 - \frac{B_n^2}{I_D^V - G_1 - E_A}$$

Merrifield and Phillips (5) have found a nearly linear correlation of ΔH and I_D^V for a series of methylated benzenes complexed with TCNE.

Two other correlations not discussed in Chan and Liao's paper can be theoretically derived and applied to the series of methylated benzene/TCNE complexes. These involve correlations of ΔH with hv and μ ct (the portion of the dipole moment of the complex due to the charge transfer interaction). Equation (IX) gives hv as a function I_D^V while equation (X) gives ΔH as a function I_D^V. Solving the two equations simultaneously:

(XI) $$\Delta H^\circ = W_0 - \frac{B_n^2}{\left[\frac{h\nu_{ct}^2}{4} - C_2\right]^{1/2} + \frac{h\nu_{ct}}{2}}$$

Where $C_2 = B_n^2 + B_e^2$. As discussed earlier C_2 and B_n might be expected to be constant. W_0 however might vary with the amount of Van der Waals stabilization but would be expected to exhibit an increasingly negative trend as the number of atoms in the complex increases. W_0 however can be evaluated from the charge transfer transition energy and the eigenvectors as determined from dipole measurement (4). The data of Merrifield (5) along with that of Chan and Liao (4) for ΔH and hv is graphed in Figure 2. A plot of the theoretical curve (equation (XI)) is also plotted assuming $B_n \approx 13.2$ and $C_2 \approx 555$ Kcal/mole (4).

Figure 2

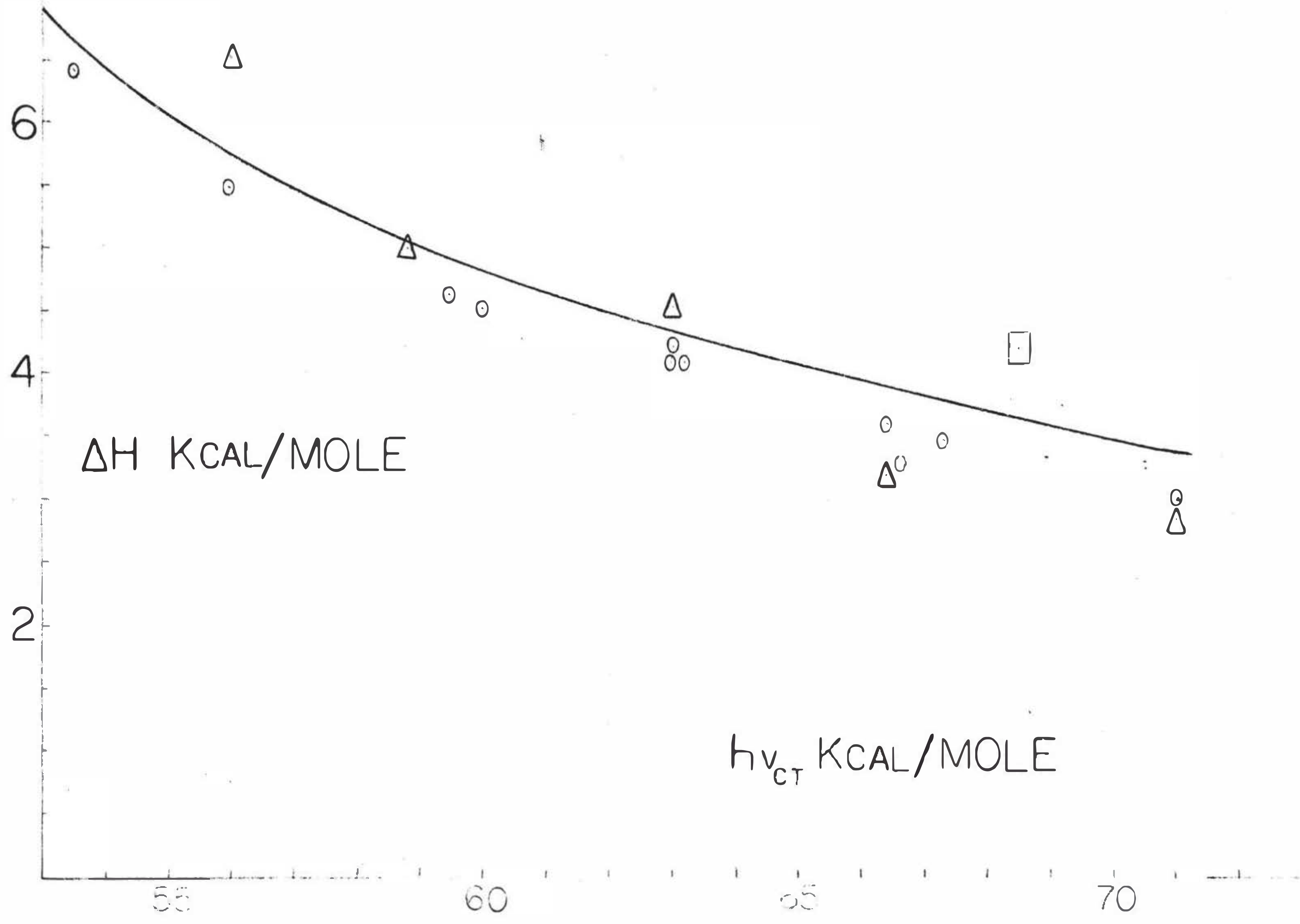
A graph of the theoretical relationship between ΔH and hv_{ct} employing empirical parameters, and depicting the data of Chan and Liao(4), and the data of Merrifield and Phillips (5).

△ = data of Merrifield

⊙ = data of Chan and Liao

□ = value for TBB/TCNE determined in this laboratory

— = theoretical curve


6
4
2
ΔH KCAL/MOLE
$h\nu_{CT}$ KCAL/MOLE
55
60
65
70

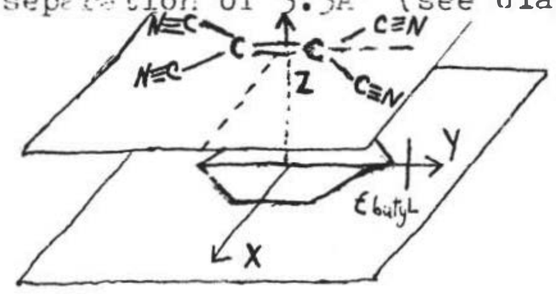
It is also possible to consider the implications of Mulliken's theory on the dipole moment of the complex. The dipole moment for the ground state (μ_n) is given by variational theory as: $\mu_n = \int \Psi_n^* |\hat{\mu}| \Psi_n \, d\tau = \int (a\Psi_0 + b\Psi_1)^* \hat{\mu} (a\Psi_0 + b\Psi_1) \, d\tau$

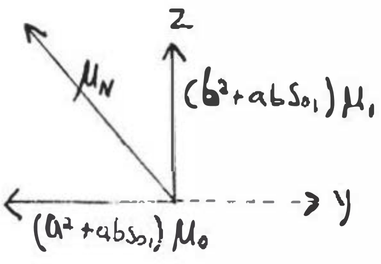
$$(XII) \quad \mu_n = a^2 \vec{\mu}_0 + b^2 \vec{\mu}_1 + 2ab \vec{\mu}_{01}$$

Where μ_0 is the quantum mechanical average for μ over Ψ_0, $\vec{\mu}_1$ is the average over Ψ_1, and $\mu_{01} = \dfrac{\int \Psi_0^* \mu \Psi_1}{a^2+b^2+2abS} = \dfrac{\int \Psi_1 \mu \Psi_0 \, d\tau}{a^2+b^2+2abS}$ (assuming μ is hermitian). μ_0 physically represents the dipole moment for the "no bond" structure or, since TCNE is nonpolar, that of the donor. μ_1 represents the dipole associated with transfer of one electron from the donor to the acceptor, μ_{01} has been approximated by Mulliken (6) as an average of the two dipoles over the overlap or $\frac{1}{2}S_{01}(\mu_0+\mu_1)$. Substituting into equation (XII):

$$(XIII) \quad \vec{\mu}_n = (a^2+abS_{01})\vec{\mu}_0 + (b^2+abS_{01})\vec{\mu}_1$$

The quantity $(b^2 + abS_{01})\mu$ is called the charge transfer dipole (μ_{ct}) where $b^2 + abS_{01}$ is the fraction of the electronic charge transfered in the bonding process. X-ray structure investigation (7) has established that complexes of TCNE with aromatic compounds have the molecular planes parallel with a separation of 3.3A° (see diagram below).





Therefore μ_0 is perpendicular to μ_1 and in terms of magnitude:

$$\mu_n^2 = (a^2+abS_{01})^2\mu_0^2 + (b^2+abS_{01})^2\mu_1^2$$

$$(XIV)\quad \mu_{ct} = (b^2+abS_{01})\mu_1$$

Both μ_0 and μ_n can be obtained from appropriate dielectric measurements. μ_1 can be calculated for the known donor-acceptor separation. Therefore with an approximation for S_{01} and application of the normalization constraints the dative and "no bond" character for the ground state (a,b) can be calculated.

Moreover, a relationship between μ_{ct} and ΔH^0 can be obtained by substituting equation (1) into the normalization requirement and finally substituting into equation (XIV). (See Appendix 4).

$$(XV)\quad \mu_{ct} = \left[\frac{W_0-\Delta H-B_n S}{W_0-\Delta H+\dfrac{B_n^2}{W_0-\Delta H}-2SB_n}\right]\mu_1$$

Since the B_n^2 term dominates the denominator a nearly linear plot of μ_{ct} versus ΔH might be expected. A plot of ΔH versus μ_{ct} for methylbenzene derivatives complexed with TCNE is given in Figure 3 from data obtained from Chan and Liao (4). A theoretical plot of equation (XV) is also plotted with the use of charge transfer parameters cited earlier.

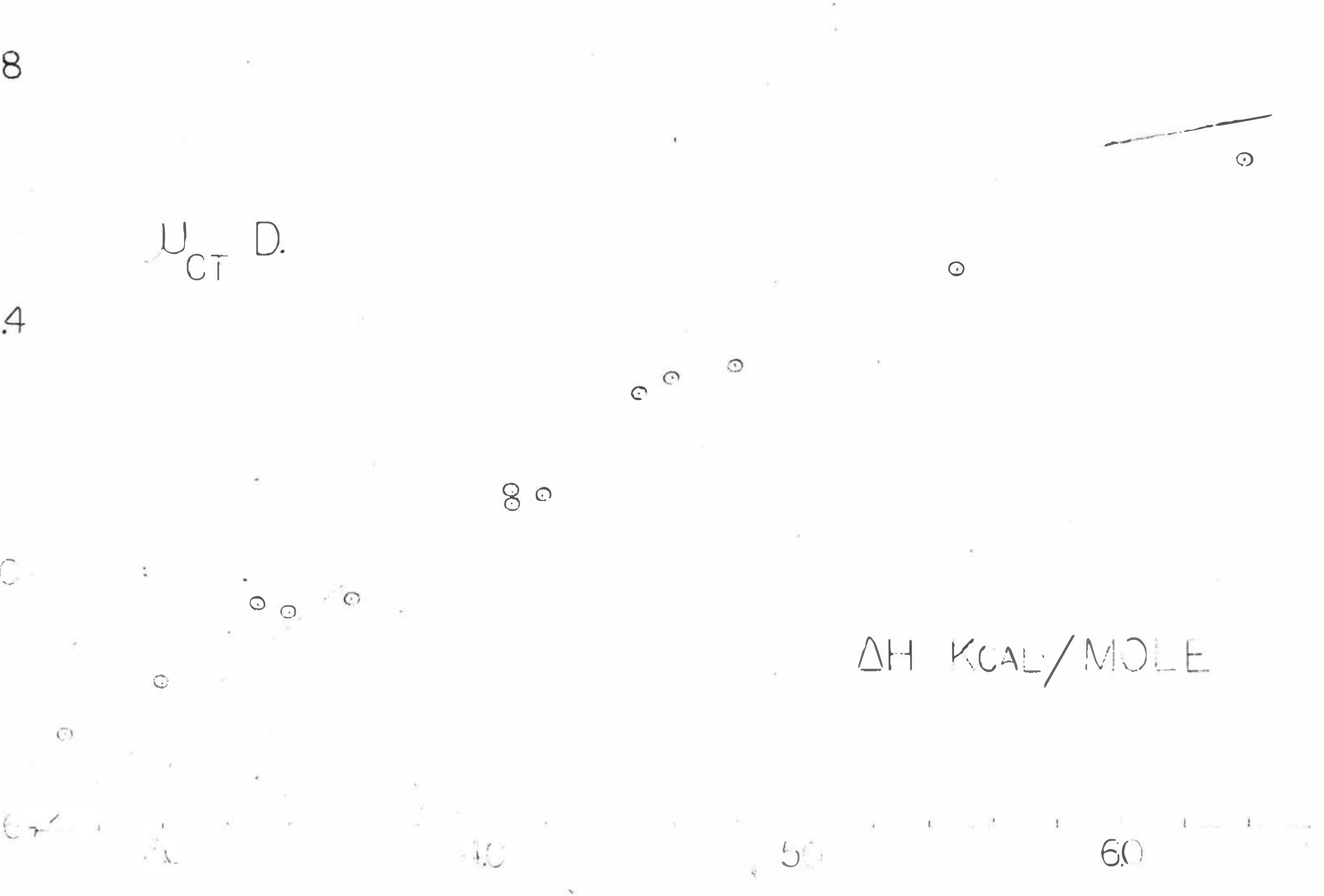
It is the purpose of this study to determine if the Mulliken parameters, that correlate the thermodynamic, dielectric and spectral properties of this series of methylated benzene/TCNE

Figure 3

Theoretical plot of ΔH versus μ_{ct} from empirical parameters and the data of Chan and Liao(4).

⊙ = data of Chan and Lialo

— = theoretical curve


8
U_CT D.
.4
ΔH KCAL/MOLE
30
40
50
60

complexes, can be extended to other benzene derivitives, particularly donors where steric factors could play an important role (e.g. t-butylbenzene).

EXPERIMENTAL

Materials

The organic materials used as solvent, donor, or dielectric standard were either Eastman Kodak Co. or J.T. Baker Analyzed and were distilled at least once through a 50cm fractionating column. Organic liquids were stored in the dark, over type 4A molecular sieve, previously heated for four hours in a tube furnace at 320°C. Criteria for purity included vapor phase chromatograms and indices of refraction. Mass spectra of t-butylbenzene showed no impurities of higher molecular weight. Table 1 provides a comparative list of experimental and literature values for the physical properties of these materials.

Tetracyanoethylene was purified by sublimation at 135°C±1° (3-4mm) yielding a white crystalline powder melting at 199-200°C in a sealed tube. TCNE was then ground to a fine powder with a motar and pestle.

Table 1

All Values Given for 25°C

Material	N_D(Lit)[a]	N_D(Exp.)	ε(Lit.)
Methylene Chloride	1.42115	1.4212	
t-butylbenzene	1.49024	1.4902	2.357[bc]
Toluene	1.49415	1.4942	2.379[c]
Benzene	1.49792	1.4979	2.275[c]
Carbon Tetrachloride	1.45739	1.4574	2.228[c]
P-Xylene	1.49325	1.4933	2.261[bc]

In Table 1 N_D refers to the index of refraction; ϵ refers to the dielectric constant. Those values with a superscript c were obtained from reference (11); those values with a superscript b were calculated from $P_m = (\epsilon - 1/\epsilon + 2)M/\rho$ where P_m refers to the molar polarizability, ϵ the dielectric constant, M the molecular weight, and ρ the density. Since P_m is constant, ϵ for a given temperature can be calculated from ϵ at another temperature and the appropriate M and ρ values.

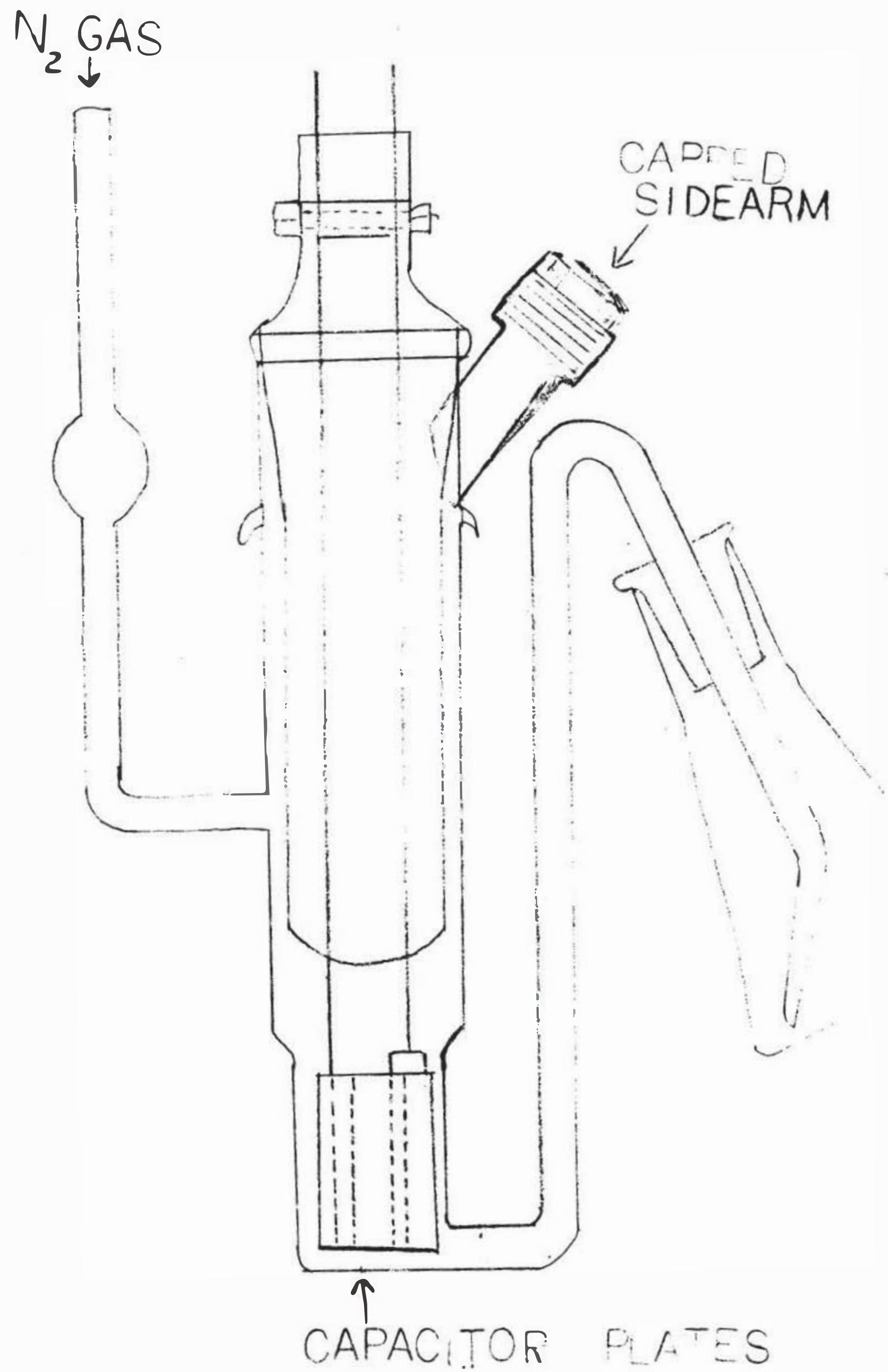
Equipment and Apparatus

U.V.-visible spectra were taken with a Beckman Acta MIV. Absorption measurements for determination of Δ H were taken with a Hitachi Perkin-Elmer 139 U.V.-visible spectrophotometer equipped with a jacketed absorption cell thermostated with a Forma-Scientific water bath. Mass spectra were taken with a Dupont 21-490 Mass Spectrophotometer. The vapor phase chromatograms were obtained from a Perkin-Elmer Model 154-L, equipped with a thermal conductivity detector and a 10 ft. column of 15% SE-30 stationary phase, with a helium carrier gas flow rate of 70-60ml/min. Indices of refraction were measured with a Bausch & Lomb Abbe refractometer. Density measurements were made with a stopper type specific gravity bottle. Weight measurements were made with a Sartorius single pan balance or a Wilkens-Anderson analytical balance. A dielectrometer, constructed in this laboratory by Mr. James Belcher, was used to obtain dielectric data by the heterodyne beat method.

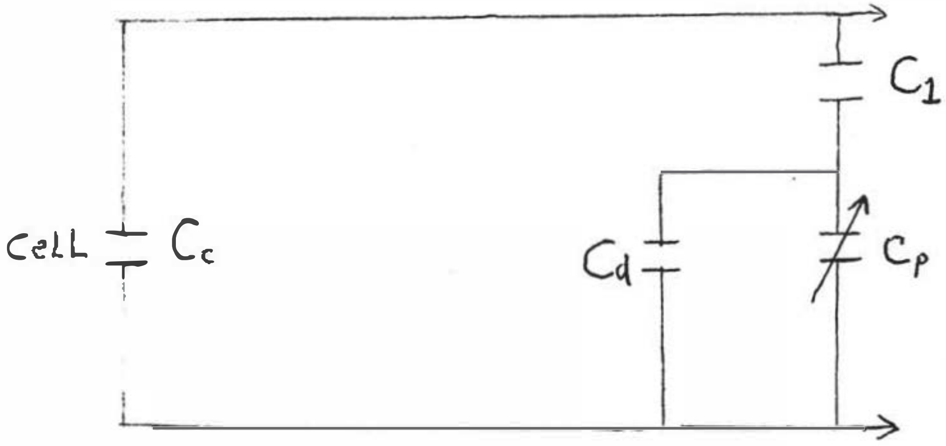
The dielectric cell (See Fig. 4), Model 2TN20LV, (capacitance 20 pf) used for pure liquid and solution measurements

Figure 4

Dielectric Cell


N$_2$ GAS
CAPPED SIDEARM
CAPACITOR PLATES

was obtained from the Balsbaugh Laboratories, Duxbury, Massachutes and was modified for this research. Materials were introduced through a capped sidearm via a 20ml volumetric pipet and evacuated by N_2 gas flow. The cell was cleaned with acetone and dried by N_2 gas flow between each reading. The following circuit diagram describes how the cell sensitivity was modified for these experiments.



Where C_c is the dielectric cell, C_p is the precision capacitor, C_1 is 200pf, and C_d is 100pf. With the fixed crystal oscillator at approximately 2.6MHz, the precision capacitor consisting of an army surplus frequency meter (Model # BC221N) was tuned to a specified null point for the beat frequency. Changes in the cell capacitance were thereby monitored by the dial null point settings. A warming up period of 10-12 hours was required to minimize frequency shifts due to thermal effects. A five minute period was necessary for the liquid to reach temperature equilibrium with the thermostated cell ($25.00^\circ \pm .02^\circ C$).

Experimental Procedure

A. Spectroscopic Studies

The solutions for electronic spectra and absorption measurements were prepared by delivering approximately 1ml of stocksolution of TCNE (.1g TCNE / 100ml CH_2Cl_2) from a capped buret. The methylene chloride was evaporated from the flask by N_2 gas flow and a weighed portion of t-butylbenzene was added. The resulting solution was diluted to 10ml with CCl_4 in a volumetric flask at 25°C. Digitalized spectra were taken of the charge-transfer complex, TCNE, and t-butylbenzene. The solutions were prepared such that the concentration of TCNE and t-butylbenzene were the same as that in the solution used to take the charge-transfer spectrum.

Absorption data for six solutions of differing molecular complex concentration were taken at various temperatures. The Bensi-Hildebrand equation (10) was used to obtain the equilibrium constant and molar extinction coefficient for the complex over a range of temperatures.

$$\frac{(\text{t-butylbenzene})(\text{TCNE})}{\text{absorption}} = \frac{(\text{t-butylbenzene})}{\varepsilon\,l} + \frac{1}{K\varepsilon l} \quad \text{(See Appendix 2)}$$

( ) =molar concentration prior to equilibrium

If the left hand side of this equation is plotted versus (t-butylbenzene) a linear graph with slope $1/\varepsilon l$ and intercept $1/K\varepsilon l$ is obtained. The equilibrium constant is evaluated from the slope over the intercept.

B. Dipole Measurements

Solutions for dipole measurements of t-butylbenzene (μ_o) were prepared from weighed portions of t-butylbenzene and CCl_4.

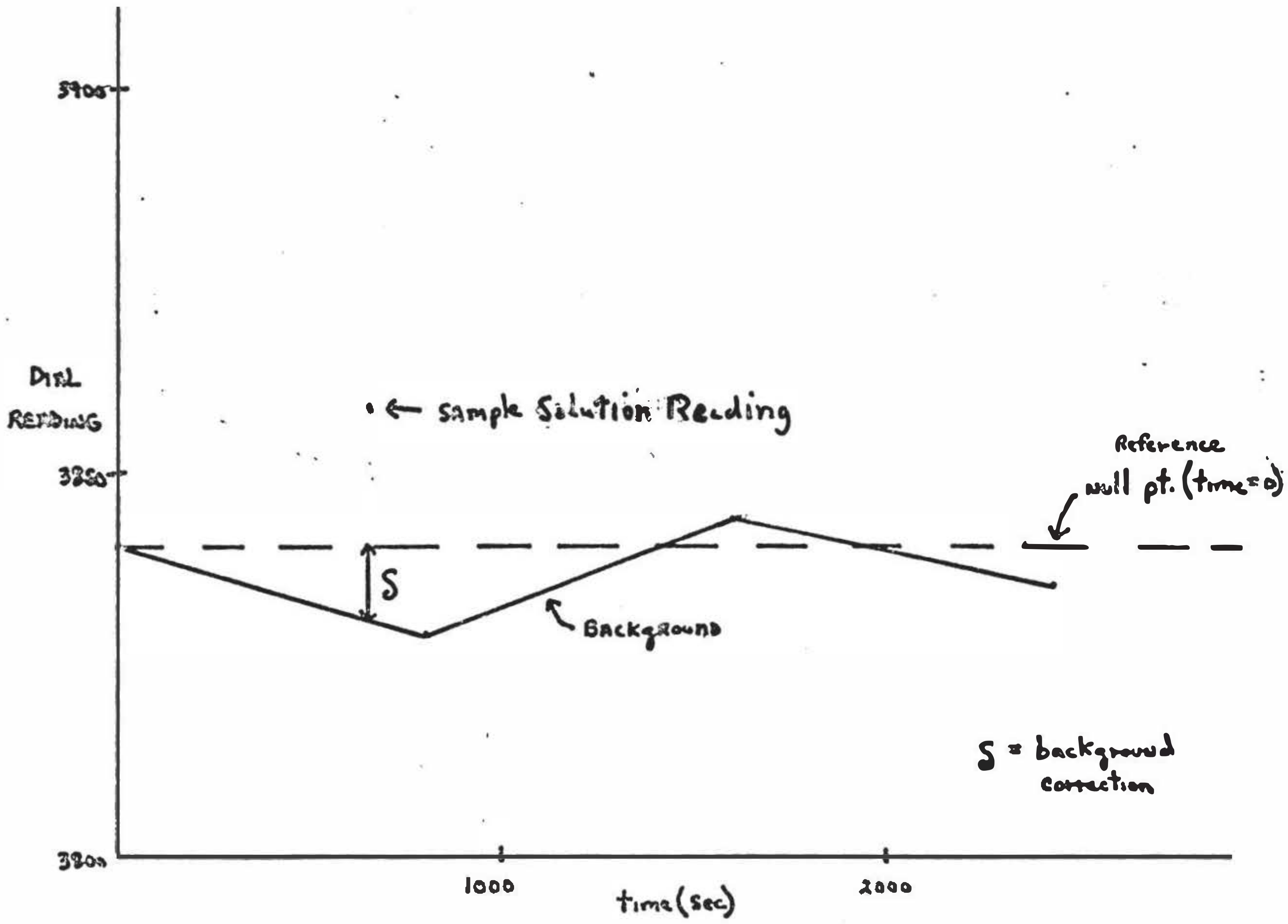
Solutions for dipole measurements of the charge transfer complex were prepared by dilution with t-butylbenzene of a saturated stock solution prepared by stirring TCNE in t-butylbenzene for four days. One ml of each of these solutions was removed with a volumetric pipette and diluted to 25ml with CCl_4. The absorption values of the resulting solutions were measured at 25°C. The concentrations of the solutions were calculated from the equilibrium constant and molar extinction coefficient previously determined by spectroscopic studies.

Since these experiments required measuring very small changes in the dielectric constant, on the order of 10^{-3}, it was necessary to correct for any background drift in the frequency of the radio frequency oscillator due to changes in atmospheric conditions, line voltage,etc. This was accomplished by observing the null point for the cell filled with CCl_4 or tolune before and after each sample measurement. All measurements were then plotted with time and the appropriate drift corrections made. A positive deviation in the background was subtracted from the observed null point dial setting. (See Figure 5)

Dielectric measurements were made on solutions of differing concentration and a series of materials of known dielectric constant. The materials of known dielectric constants were used to obtain a calibration curve to convert dial settings to dielectric constants. For both experiments this calibration curve was a linear function over the range in which the solutions varied. The dipole moment was calculated from the slopes (a,b) of the plots of dielectric constant and density versus mole fraction by the Headstrand equation. (See appendix 1)

Figure 5

Dielectrometer Background Correction


3900
DIAL
READING
3850
3800
• ← Sample Solution Reading
Reference
null pt. (time=0)
S
Background
S = background
correction
1000
time (sec)
2000

Results

Spectroscopic Studies

Figure 6 provides a composite spectrum of TCNE, t-butylbenzene the charge transfer complex. Neither TCNE nor t-butylbenzene exhibited any absorption in the range of the complex.

The data in Table 2 was fit to the Benesi-Hildebrand equation by a linear least squares program. K_{eq} was then calculated from the slope and intercept.

$$\frac{(\text{t-butylbenzene})(\text{TCNE})}{\text{Absorption}} = \frac{(\text{t-butylbenzene})}{\varepsilon \ell} + \frac{1}{K\varepsilon \ell}$$

() = molar concentrations

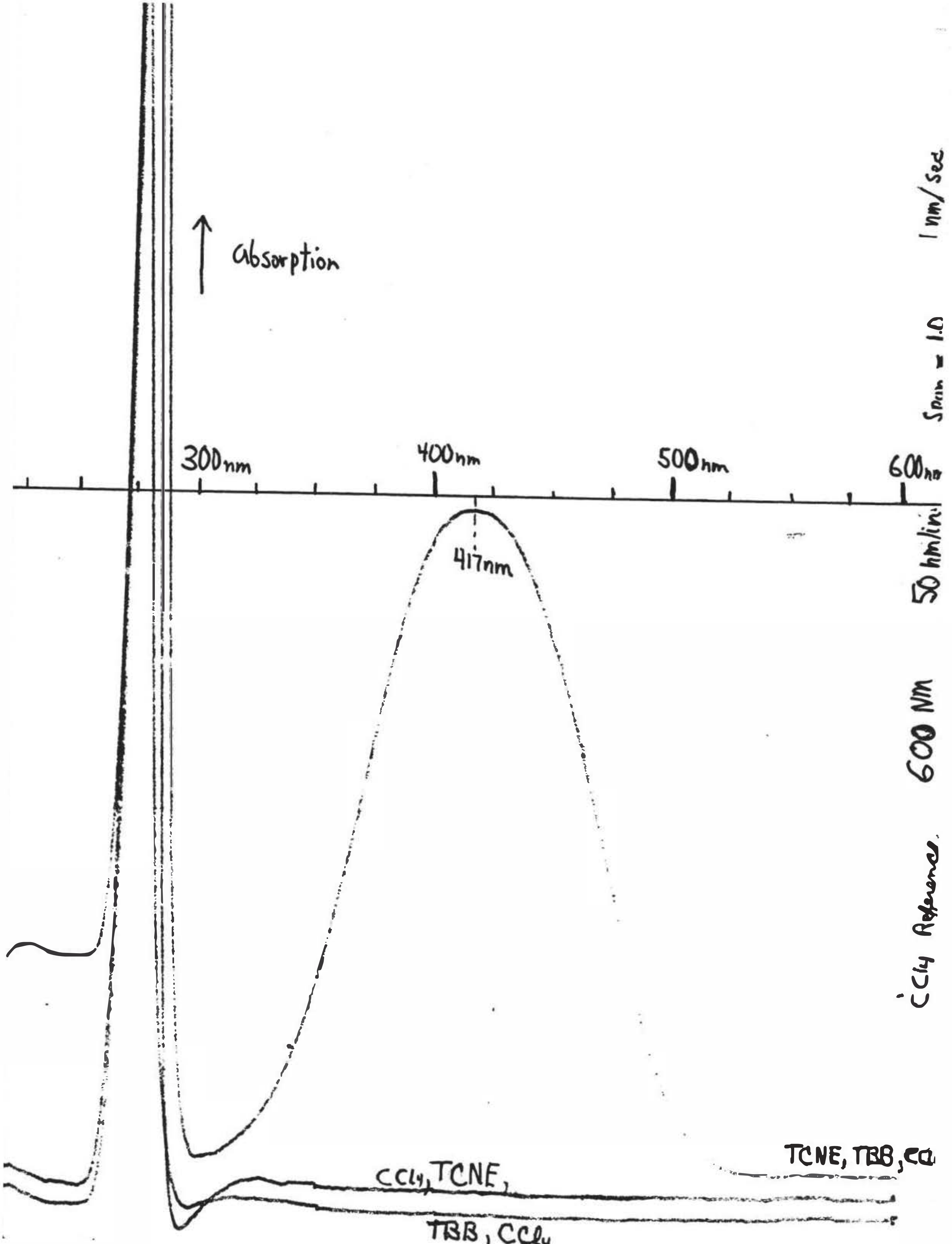
Table 2 Measurements made at 417nm

		absorption						
(TBB)	(TCNE)	6.2°C	26.0°C	24.8°C	34.7°C	44.3°C	54.8°C	64.4°C
.3515	7.68×10^{-4}	.437	.357	.315	.268	.236	.203	.177
.0964	7.92 "	.137	.118	.111	.096	.079	.071	.061
.5552	8.00 "	.623	.539	.472	.415	.368	.320	.284
.7490	7.76 "	.733	.642	.569	.504	.456	.398	.349
.9120	8.00 "	.870	.796	.688	.620	.561	.499	.444
1.027	7.84 "	.896	.818	.708	.640	.582	.520	.457

The plots for this data are seen in Figures 7-13 and the results tabulated in Table 3.

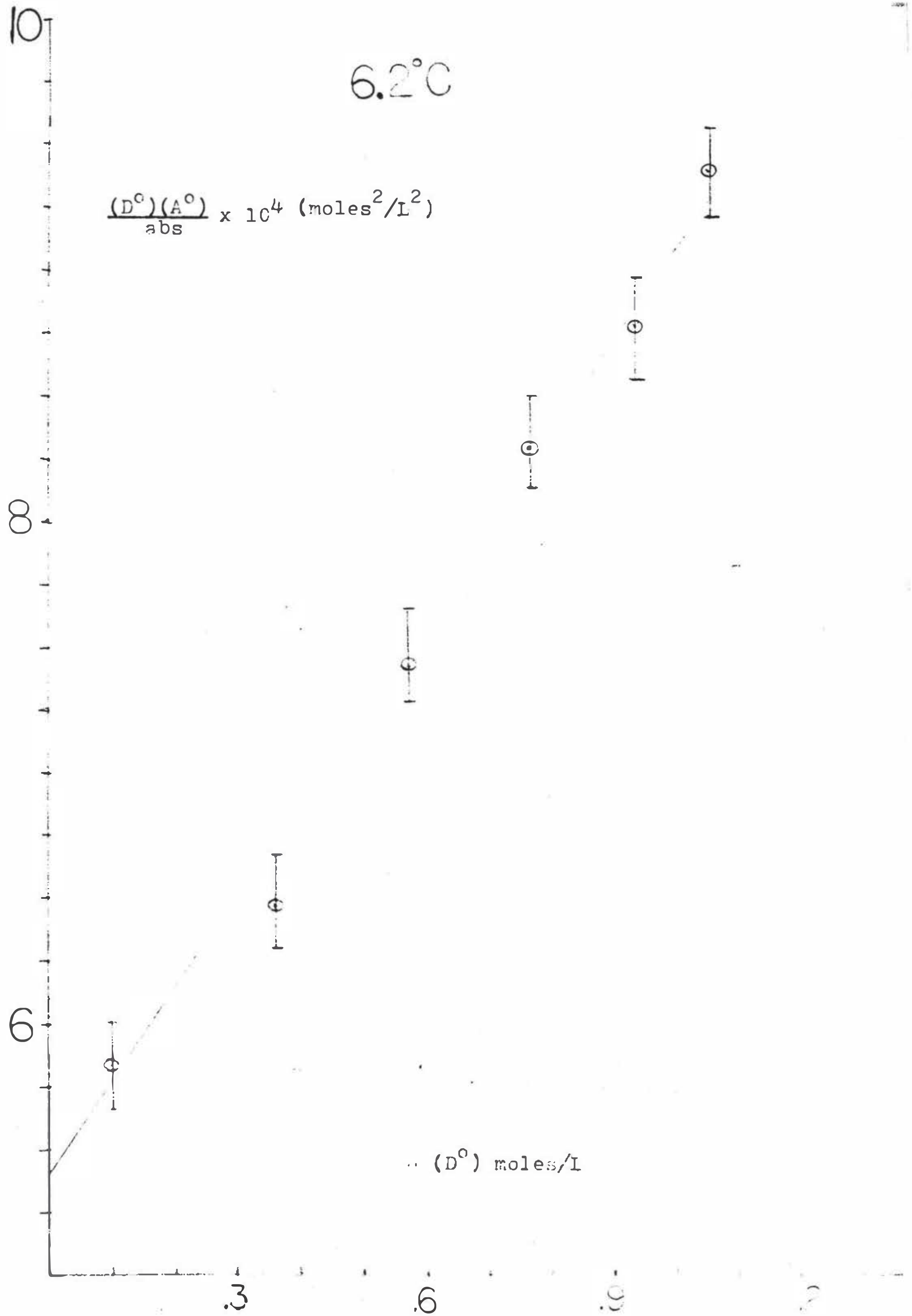
Figure 6

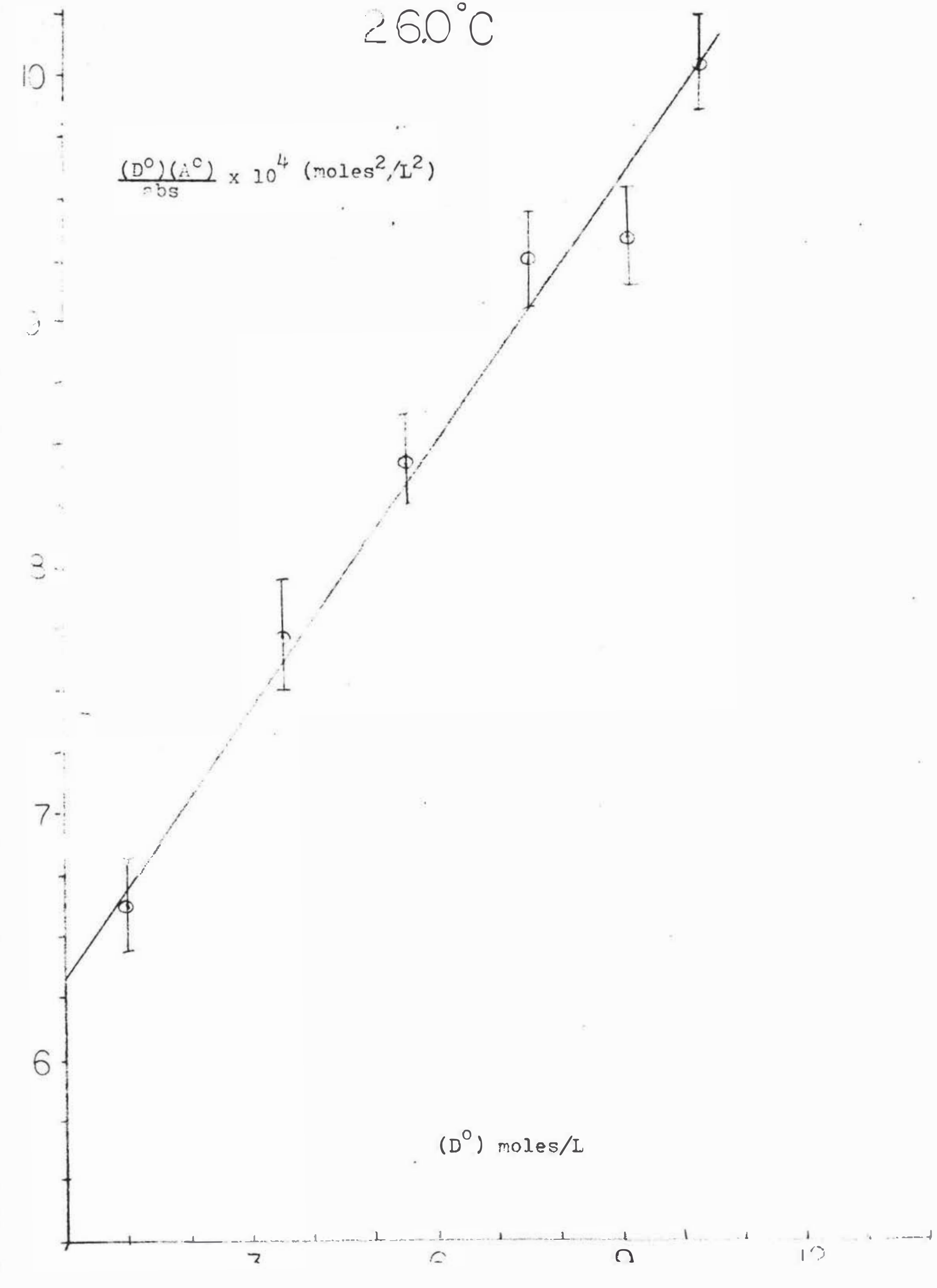
Composite spectrum of TCNE, TBB, and molecular complex in uv-visible range.

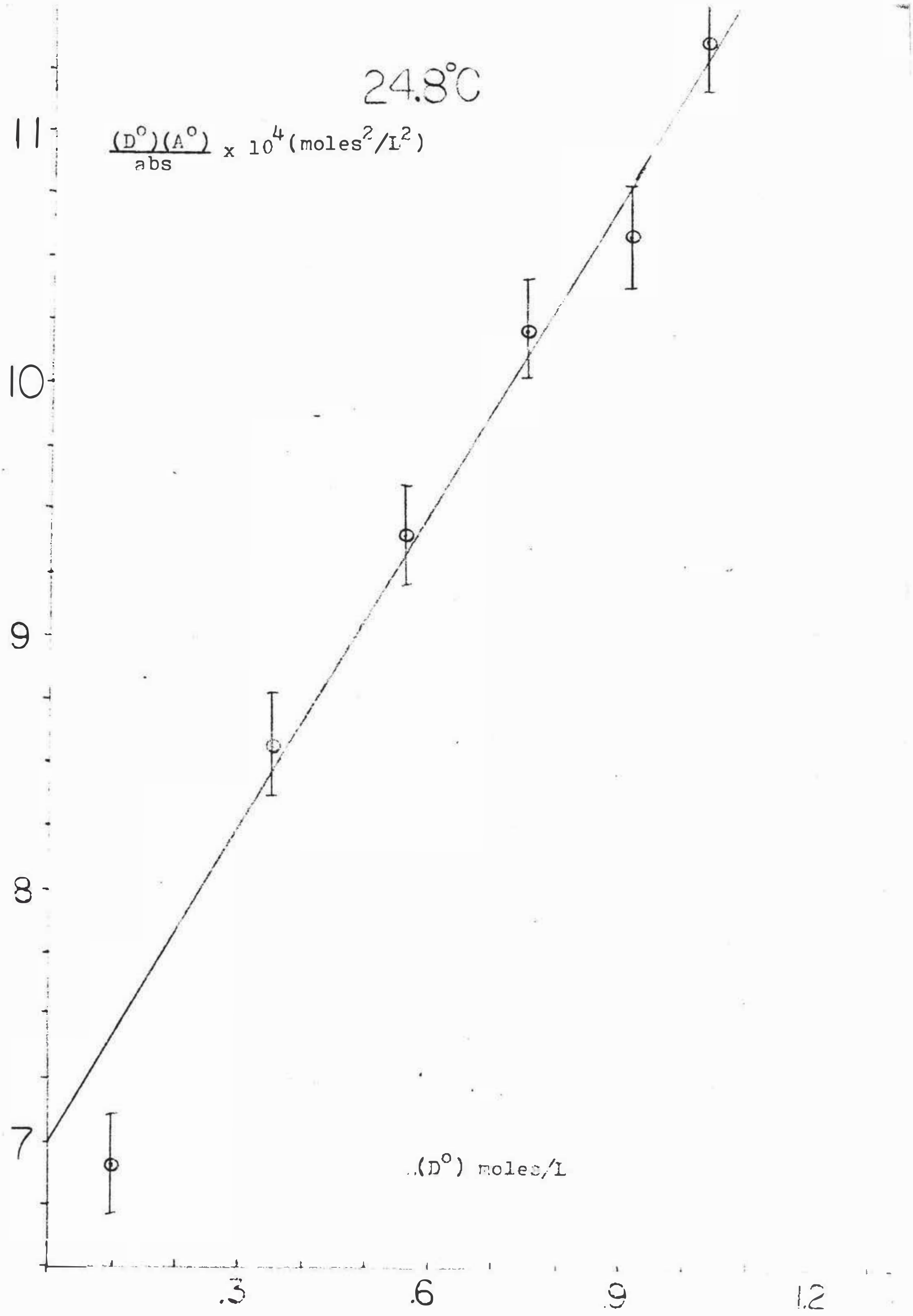

absorption
300nm
400nm
500nm
600nm
417nm
TCNE, TBB, CCl4
CCl4, TCNE,
TBB, CCl4
1 nm/sec
Span = 1.0
50 nm/in
600 NM
CCl4 Reference

Figures 7-13

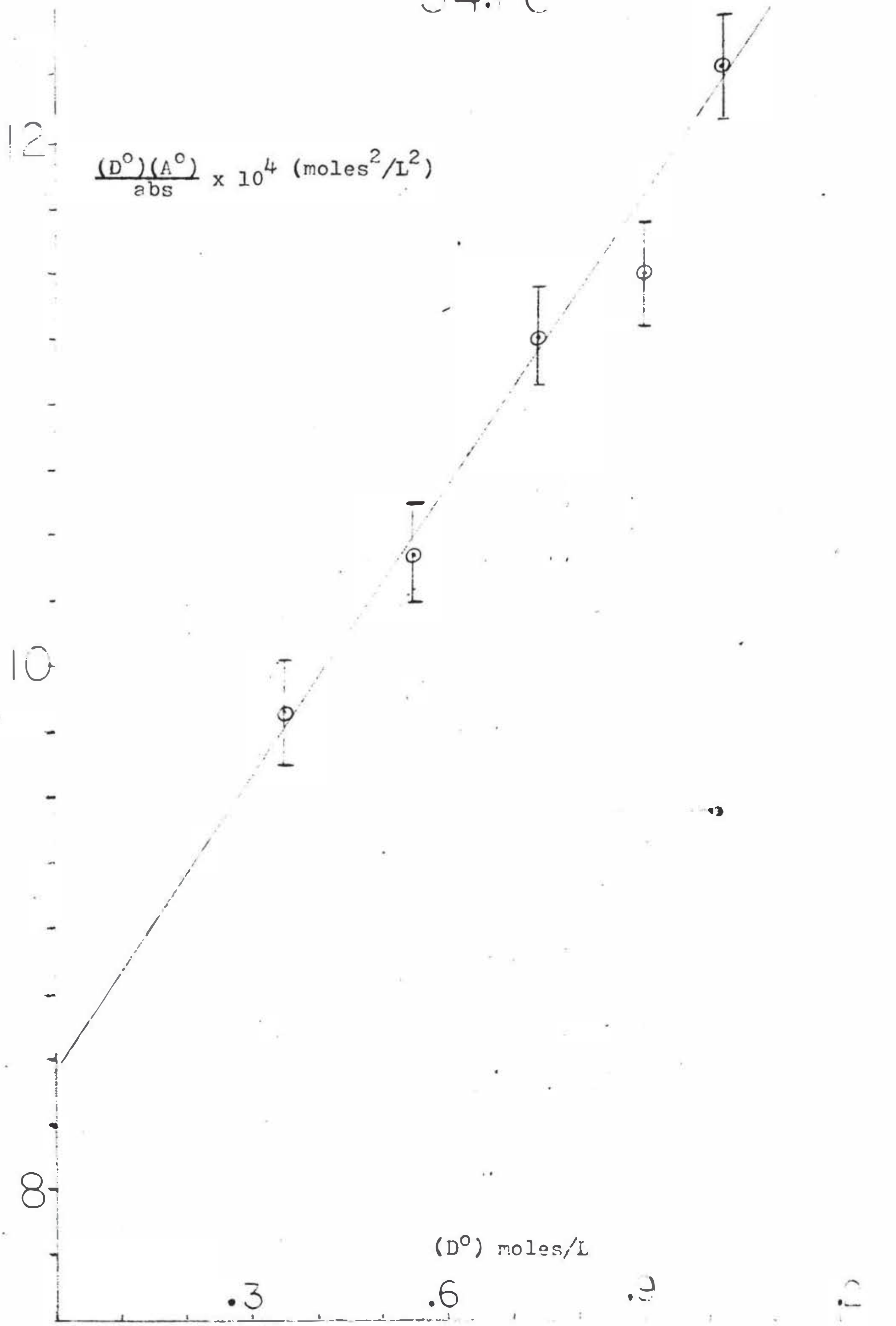
Plots of $(D^o)(A^o)$/abs versus (D^o) for molecular complex at various temperatures. Error bars evaluated from uncertainty in weight and volume measurements and a sample calculation.

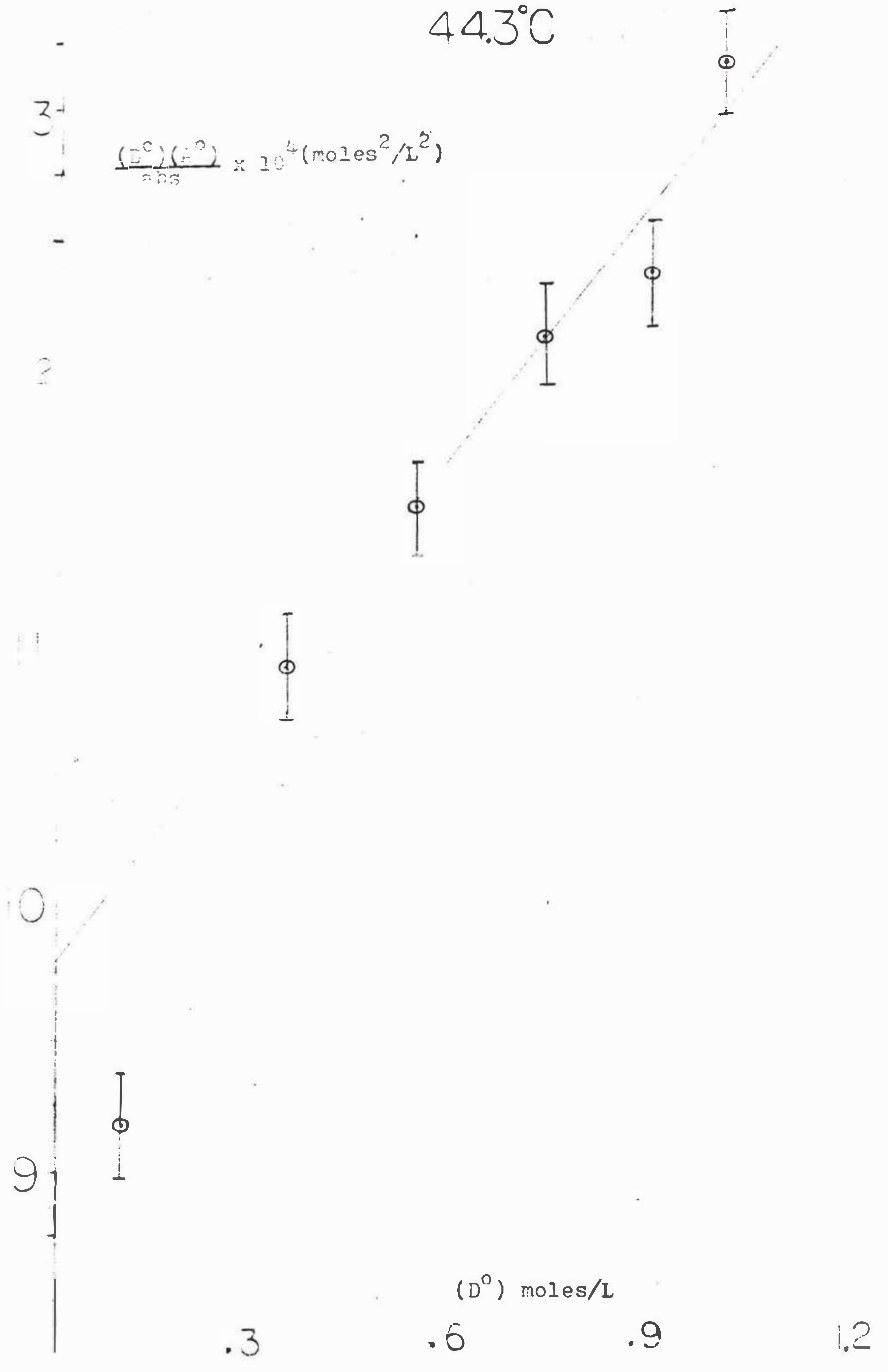

10
6.2°C
$\frac{(D^{o})(A^{o})}{abs}$ x 10^{4} (moles^{2}/L^{2})
8
6
(D^{o}) moles/L
.3
.6
.9

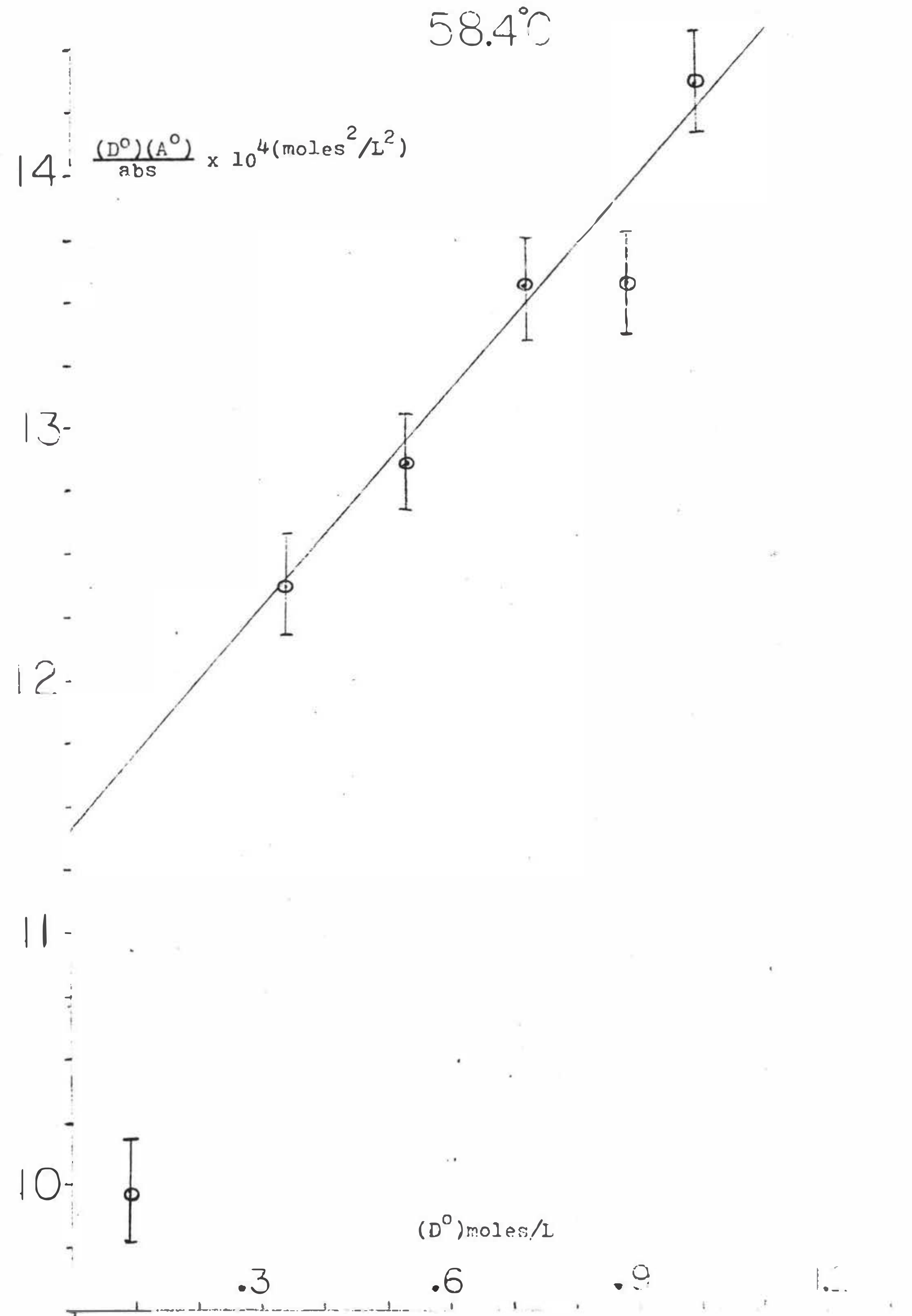

260°C
$\frac{(D^o)(A^c)}{abs} \times 10^4$ (moles^2/L^2)
10
8
7
6
(D^o) moles/L
7


24.8°C
(D°)(A°)/abs x 10⁴(moles²/L²)
11
10
9
8
7
(D°) moles/L
.3
.6
.9
1.2

34.7°C




44.3°C


58.4°C
$\frac{(D^o)(A^o)}{abs}$ x 10^4(moles^2/L^2)
14
13
12
11
10
(D^o)moles/L
.3
.6
.9

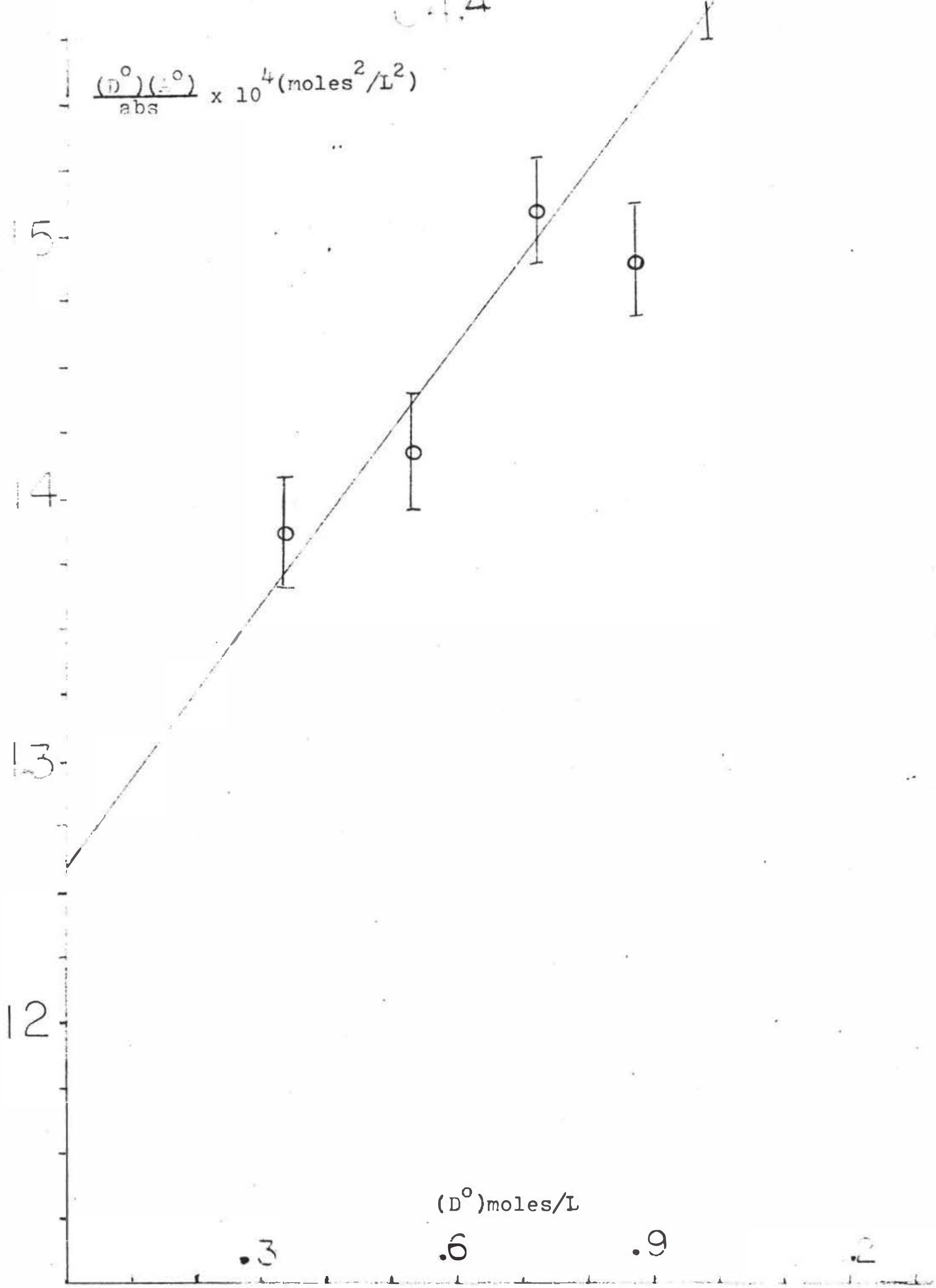

(D°)(A°)/abs x 10⁴(moles²/L²)
15
14
13
12
(D°)moles/L
.3
.6
.9
.2

Table 3

Values listed for 417nm

Temp.	Molar Equilibrium Constant	Molar Extinction Coefficient
6.2°C	.814	2431 (L/mole-cm)
26.0 "	.499	3036 "
24.8 "	.553	2520 "
34.7 "	.412	2832 "
44.3 "	.330	3104 "
54.8 "	.250	3521 "
64.4 "	.232	3369 "

The free energy of formation is given by :

$$\Delta G = \Delta G^{o} - RT\ \ln Q = \Delta H - T\Delta S$$

where Q is the product/reactant ratio. At equilibrium ΔG is zero and Q becomes the equilibrium constant K_{eq} Therefore:

$$-\Delta H/RT + C = \ln K \quad \text{where } C = \Delta S/R + \Delta G^{o}$$

According to the equation above, a plot of 1/T versus lnK has a slope of $\Delta H/R$. Figure 14 shows this plot for the data above. ΔH was found to be $\underline{4.2 \pm .4}$Kcal/mole by a linear least squares fit of 1/T versus lnK from the data of Table 3.

Dipole Measurements of t-butylbenzene

The dielectrometer null point dial settings were calibrated in terms of dielectric constant from the dial setting for materials of known dielectric constant appearing in Table 4. The calibration curve appears in Figure 15.

The data of Table 5 was used to obtain the slopes of the linear plots of dielectric constant and density versus mole-fraction. These plots appear in Figures 16 and 17.

Table 4

Calibration standards for t-butylbenzene dipole measurements

Material	Dial Setting	ε(Literature)(25°C)
CCl_4	384	2.228
P-xylene	805	2.2608
Benzene	958	2.275

Table 5

Solution data for t-butylbenzene in CCl_4

Solution	Density	Mole fraction TBB	Dial Setting	ε
1	1.54602	.02995	464	2.2343
2	1.52654	.04830	511	2.2380
3	1.48517	.08920	602	2.2454
4	1.46150	.10880	658	2.2498
5	1.42450	.14830	755	2.2576

Dielectric constants and densities of solutions exhibit the expected linear relationship to mole fraction of solute.

$$\varepsilon_{12} = a\bar{X}_2 + \varepsilon_1$$

$$\rho_{12} = b\bar{X}_2 + \rho_1$$

where ε_{12} is dielectric constant of solution, $\bar{X}_2$ is mole fraction of solute, ε_1 is dielectric constant of solvent, ρ_{12} is the solution density, and ρ_1 is the density of the solvent.

a and b, known as the Headstrand parameter, were evaluated from a least squares fit and used in the following equations to calculate the dipole moment of the solute.

Figure 14

ln (K_{eq}) versus 1/T for molecular complex
Error bars evaluated from slope analysis of the plots of (D^o)(A^o)/abS versus (D^o) and the uncertainty in temperature.

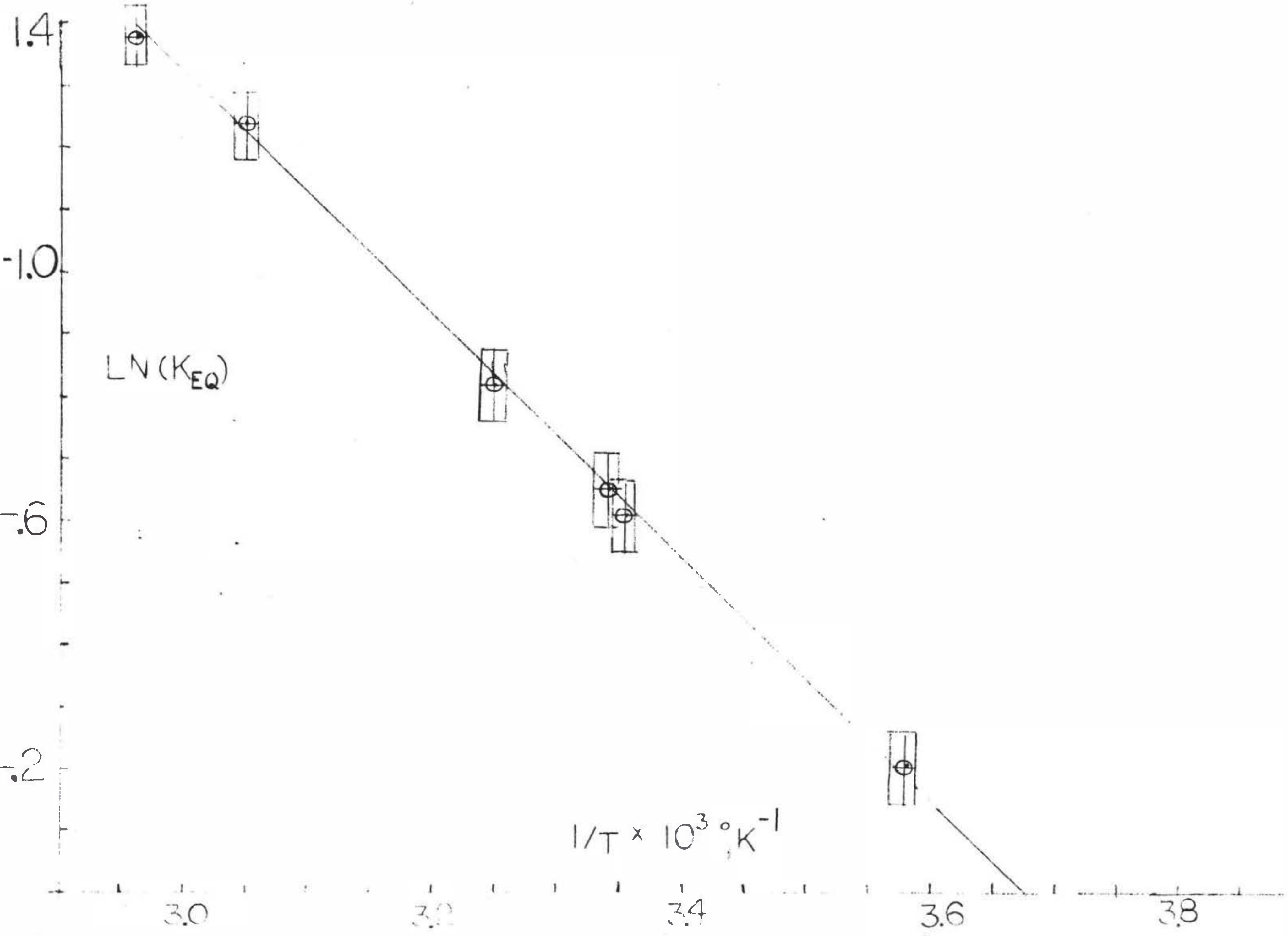

1.4
1.0
.6
.2
LN (K_{EQ})
1/T × 10^3 °K^{-1}
3.0
3.2
3.4
3.6
3.8

Figure 15

Dielectric constant versus dial setting.
Calibrated function for dipole measurements of
TBB in CCl_4.

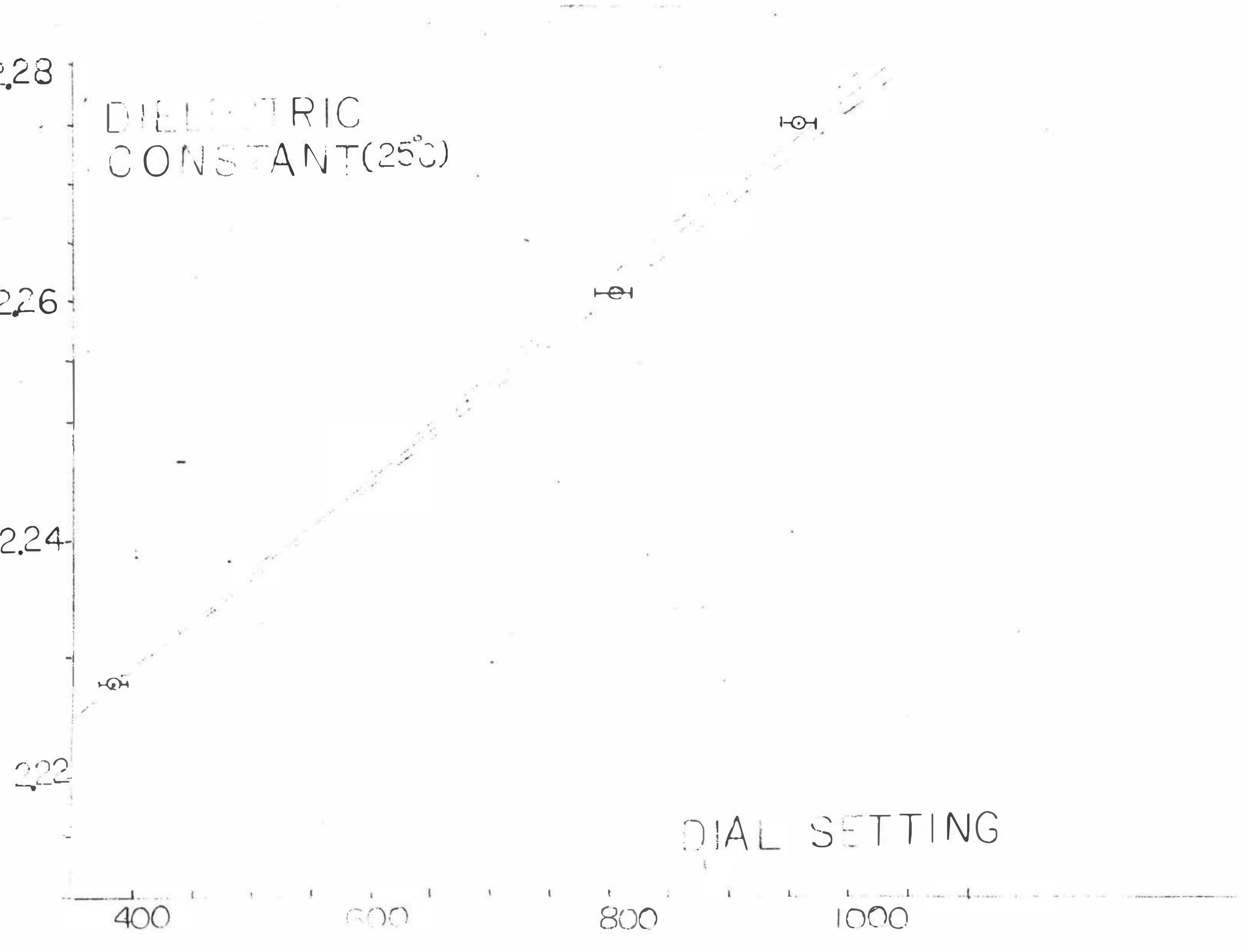

DIELECTRIC
CONSTANT(25°C)
2.28
2.26
2.24
2.22
DIAL SETTING
400
600
800
1000

Figure 16

Plot of dielectric constant versus mole fraction for TBB in CCl_4.

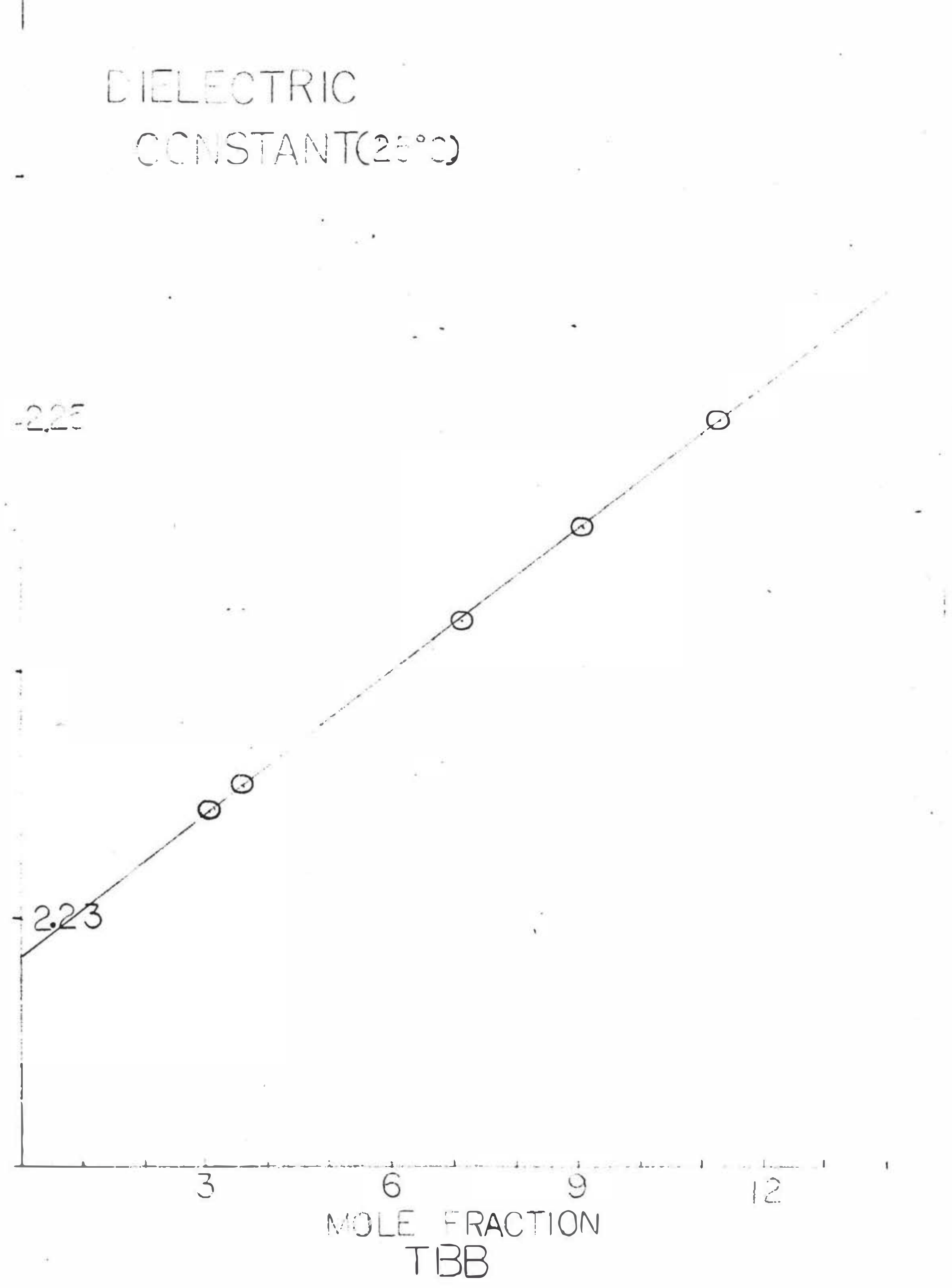
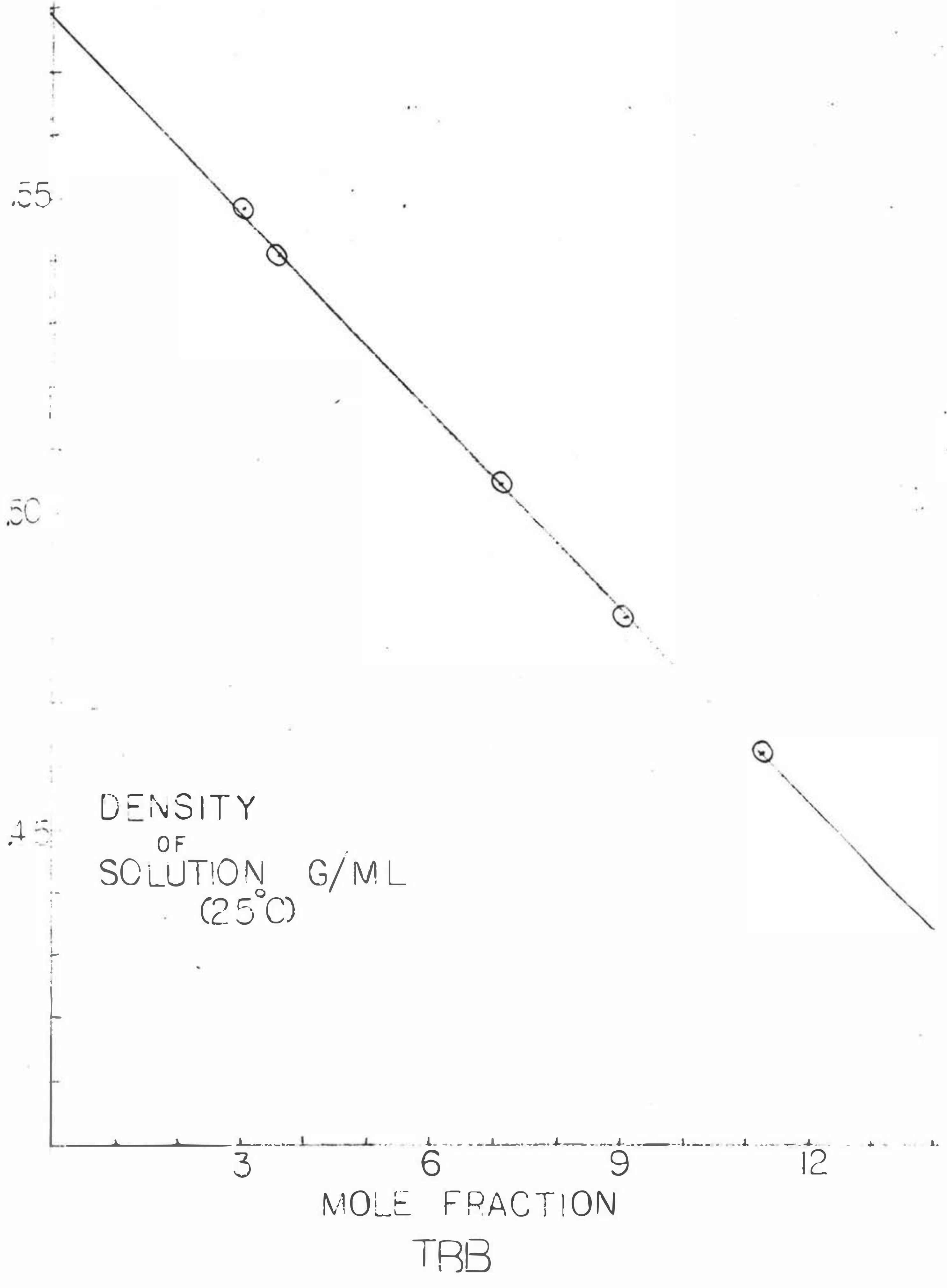

DIELECTRIC
CONSTANT(25°C)
2.25
2.23
3
6
9
12
MOLE FRACTION
TBB

Figure 17

Plot of density versus mole fraction for TBB in CCl_4.


.55
.50
.45
DENSITY
OF
SOLUTION G/ML
(25°C)
3
6
9
12
MOLE FRACTION
TRB

$$P_{2m} = \frac{3M_1 a}{(\varepsilon_1+2)^2 \rho_1} + \frac{\varepsilon_1 - 1}{(\varepsilon_1+2)\rho_1} \left(M_2 - \frac{M_1 b}{\rho_1} \right) \quad \text{(See Appendix I)}$$

$$P_{2d} = \left(\frac{n_2^2 - 1}{n_2^2 + 2} \right) \frac{M_2}{\rho_2}$$

$$P_{2\mu} = \frac{4\pi N_0 \mu^2}{9kt} = P_{2m} - P_{2d}$$

Where P_{2m} is the molar polarization of solute, P_{2d} is the distortion polarization, M_2 is the molecular weight of solute, n_2 is the index of refraction of solute, M_1 is the molecular weight of the solvent, ε_1 is the dielectric constant of the solvent, ρ_1 is the density of the solvent, N_0 is Avagadro's number, k is Boltzman's constant, T is the temperature, and μ is the dipole moment.

Values used in calculation are as follows:

M_1 = 153.8 g/mole

M_2 = 134.22 g/mole

a = .2006

b = -1.03 g/ml

n = 1.49024

ρ_2 = .86240 g/ml

ρ_1 = 1.58439 g/ml

ε_1 = 2.228

Results are as follows:

P_{2m} = 46.27 cc

P_{2d} = 45.01 cc

$P_{2\mu}$ = 1.26 cc

μ = .25 ± .01 Debye

Dipole Measurements of the Charge Transfer Complex

The dielectrometer null point settings were calibrated in terms of dielectric constant from the dial settings for materials of known dielectric constant appearing in Table 6. The calibration curve appears in Figure 18.

The data of Table 7 was used to obtain the slopes of the plots of dielectric constant and density versus mole fraction. These plots appear in Figures 19 and 20. The nonlinearity of the graph of dielectric constant of solution versus mole fraction of t-butylbenzene/TCNE complex prevented the calculation of a dipole moment for the complex.

Table 6

Calibration Data for t-butylbenzene/TCNE Measurements

Material	Dial Setting	Dielectric Constant (Literature)
t-butylbenzene	2860	2.357
benzene	811	2.275
toluene	3360	2.379

Table 7

Solution Data for t-butylbenzene/TCNE Solutions

Solution	Mole Fraction CT	Dial Setting	Density	Dielectric Constant
1	6.6×10^{-4}	3062.0	.8596	2.3656
2	15.1×10^{-4}	3216.0	.8601	2.3726
3	31.6×10^{-4}	3181.0	.8607	2.3710
4	39.0×10^{-4}	3167.0	.8619	2.3704
5	50.5×10^{-4}	3141.0	.8622	2.3692

Figure 18

Calibration function for dielectric constant versus dial setting for charge transfer complex in TBB.

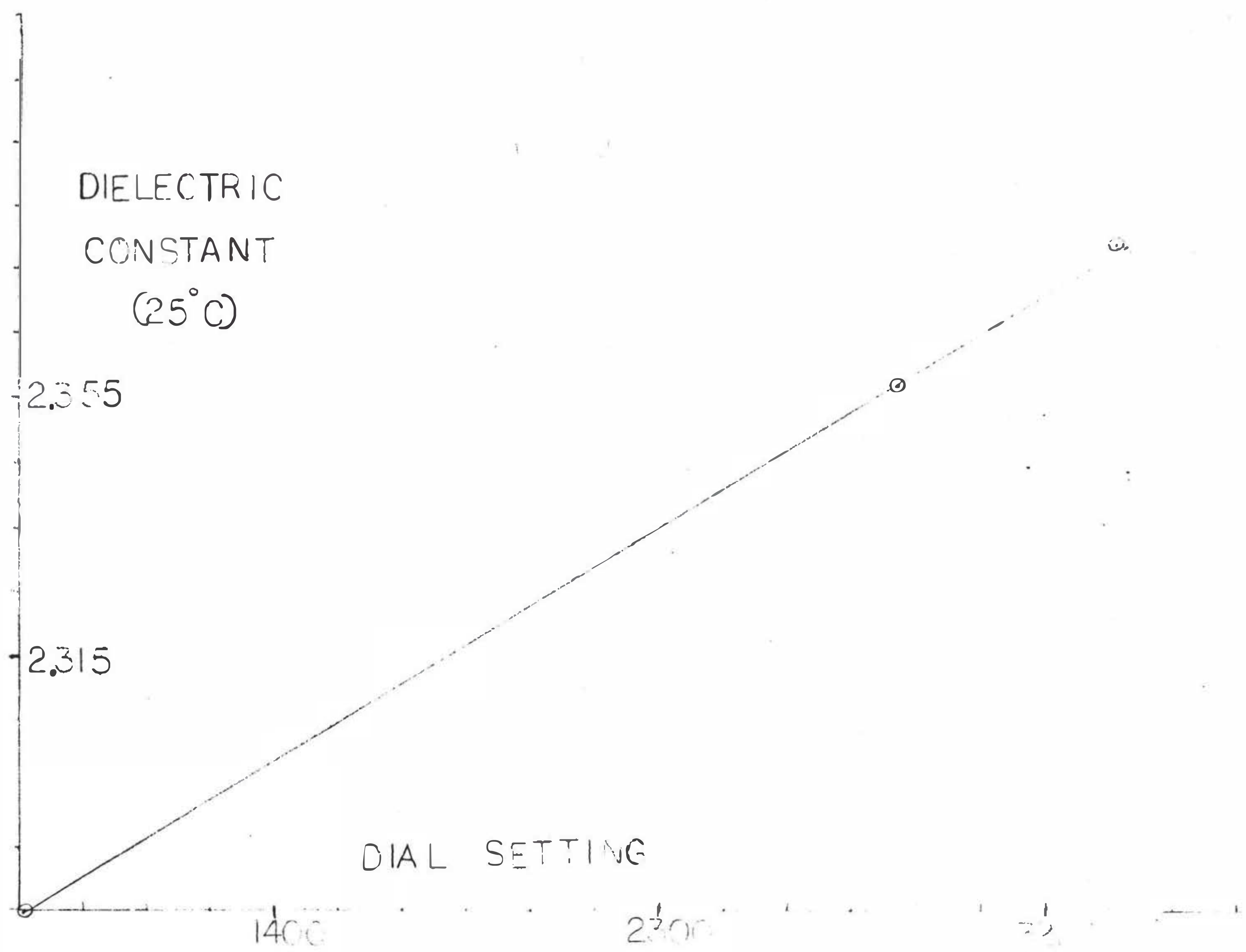

DIELECTRIC
CONSTANT
(25°C)
2.355
2.315
DIAL SETTING
1400
2300

Figure 19

Graph of density versus mole fraction for charge transfer complex in TBB.

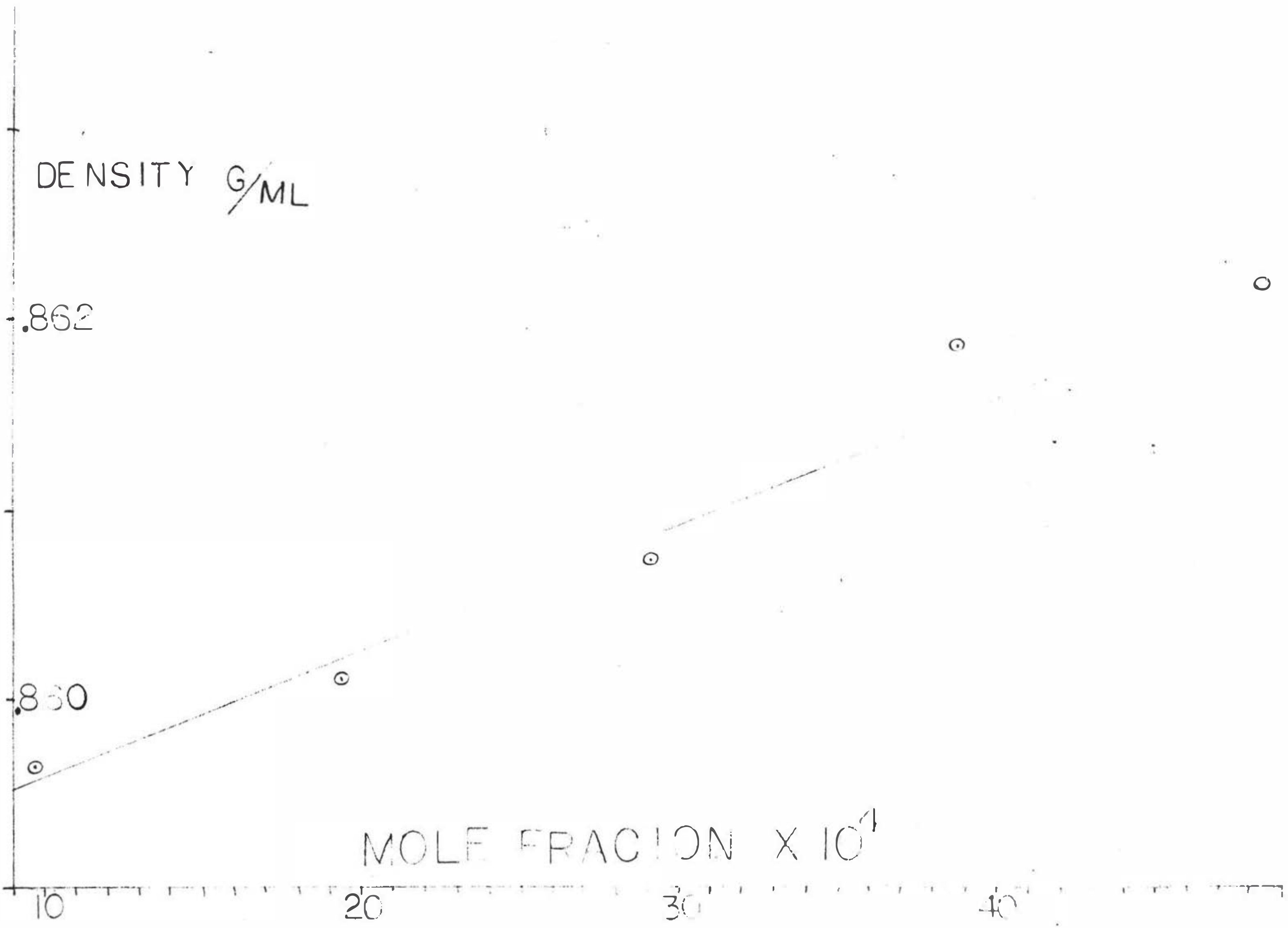
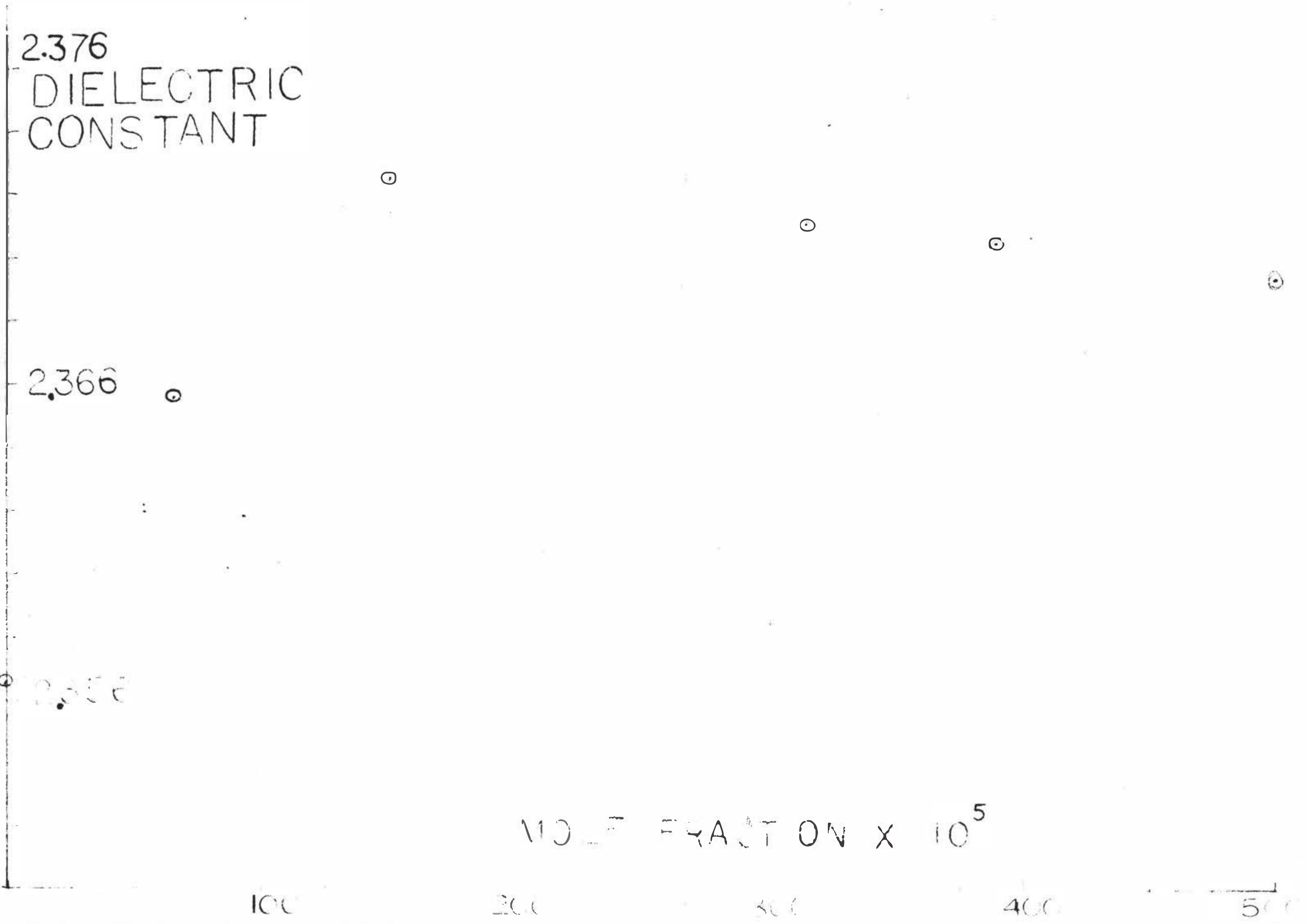

DENSITY G/ML
.862
.860
MOLE FRACTION X 10^{-1}
10
20
30
40

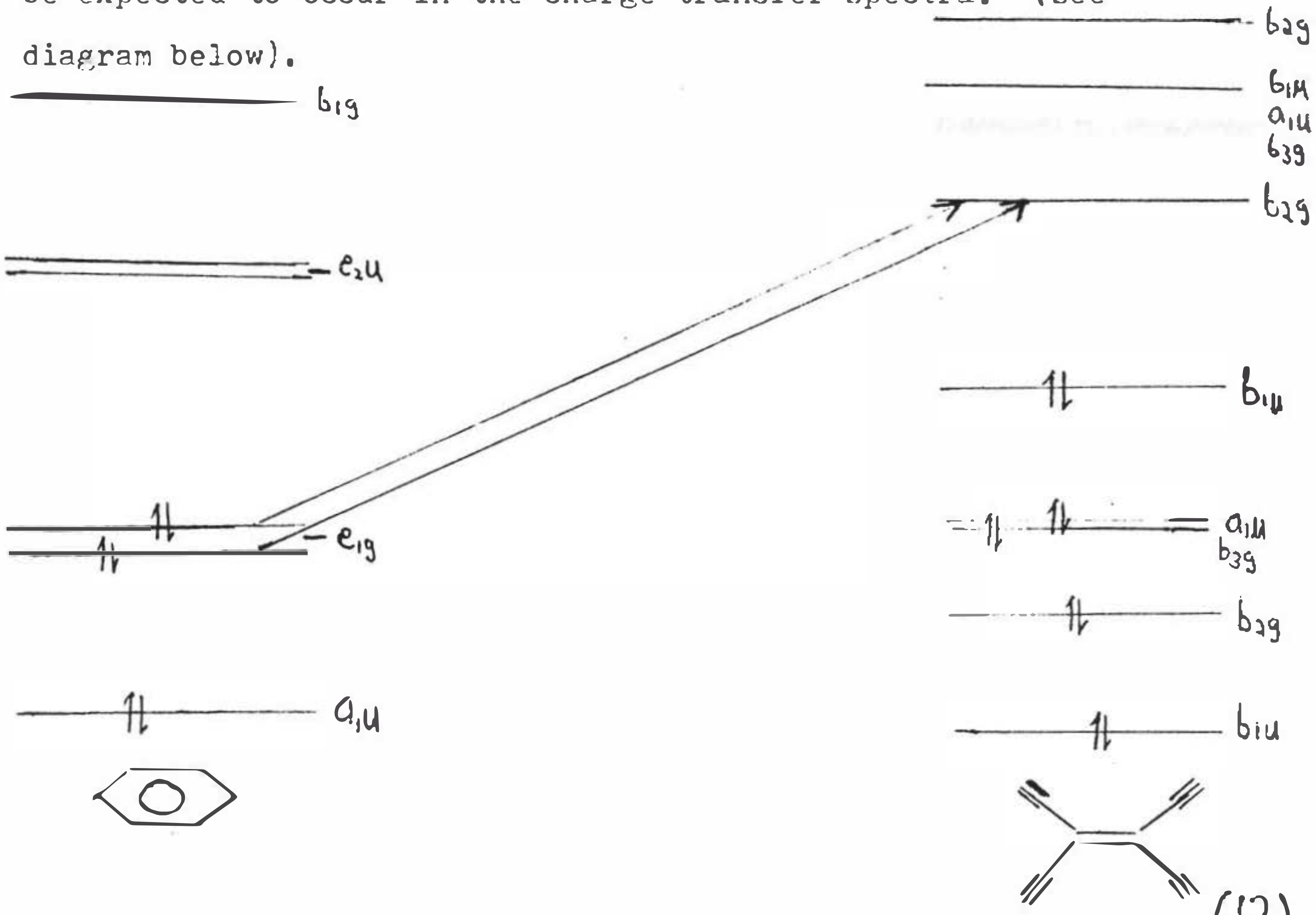
Figure 20

Plot of dielectric constant versus mole fraction for charge transfer complex in TBB.


2.376
DIELECTRIC
CONSTANT
2.366
2.356
100
200
300
400
500
MOLE FRACTION X 10^5

DISCUSSION

Since the highest filled π orbital of benzene is doubly degenerate and can be split by substitution, two features might be expected to occur in the charge transfer spectra. (See diagram below).



(12)

In a few complexes this splitting is resolved, however in general a wide unresolved band is observed. Merrifield and Phillips (5) have calculated the splittings of the E_{1g} level of benzene due to substitution and added this to the band width of the benzene/TCNE complex for several compounds. In general there was good agreement with the observed band widths. A gaussian fit of our spectra was made according to the following equation. $G = H\epsilon^{\frac{-x^2}{2\sigma^2}} = Ae^{-[(\lambda-\lambda_{max})^2/(X_h^2/\ln(2))]}$

Where A is the maximum absorption, X_h is the value of $\lambda - \lambda_{max}$ at the point where the absorption is $\frac{1}{2}A$, and λ_{max} is the wavelength of maximum absorption. The residuals between the gaussian fit and the actual spectrum indicate a nongaussian band shape. A computer plot of the gaussian, spectrum, and residuals is provided in figure 21. Using Briegleb's (8) empirical half widths relationship: $(\nu_h - \nu_l)/2(\nu_{max} - \nu_l) \approx 1.2$ Where ν_h, ν_l are the frequencies at half intensity on the high and low sides respectively. According to this equation a single value for ν_{max} as if the splitting did not occur can be calculated. ν_{max} was found to be 23,733cm^{-1} or 421nm.

The applicability of the Mulliken parameters, determined by Chan and Liao (4), to the t-butylbenzene/TCNE complex can be accessed by analyzing the correlation of ΔH with hv. Figure 22 shows a graph of the theoretical curve determined by empirical parameters from Chan and Liao, the data of Merrifield and Phillips, and the measured values for the t-butylbenzene/TCNE complex. Within experimental error, the point corresponding to the t-butylbenzene/TCNE complex exhibits no significant deviation from the theoretical plot. Therefore it can be concluded that the Mulliken parameters as determined by Chan and Liao are consistent with the t-butylbenzene/TCNE complex.

The plots of density and dielectric constant of solution versus mole fraction of t-butylbenzene show good linearity and reproducibility, although the value of .25D is lower then most listed in McClellan's book (9) for the dipole moment of t-butylbenzene.

From the correlation of ΔH versus μ_{ct} (See Fig. 3) a value of 1.21D can be predicted for the dipole moment of the t-butylbenzene/TCNE complex.

Figure 21

Computer plot of the spectrum, Gaussian fit, and the residuals for TBB/TCNE complex.

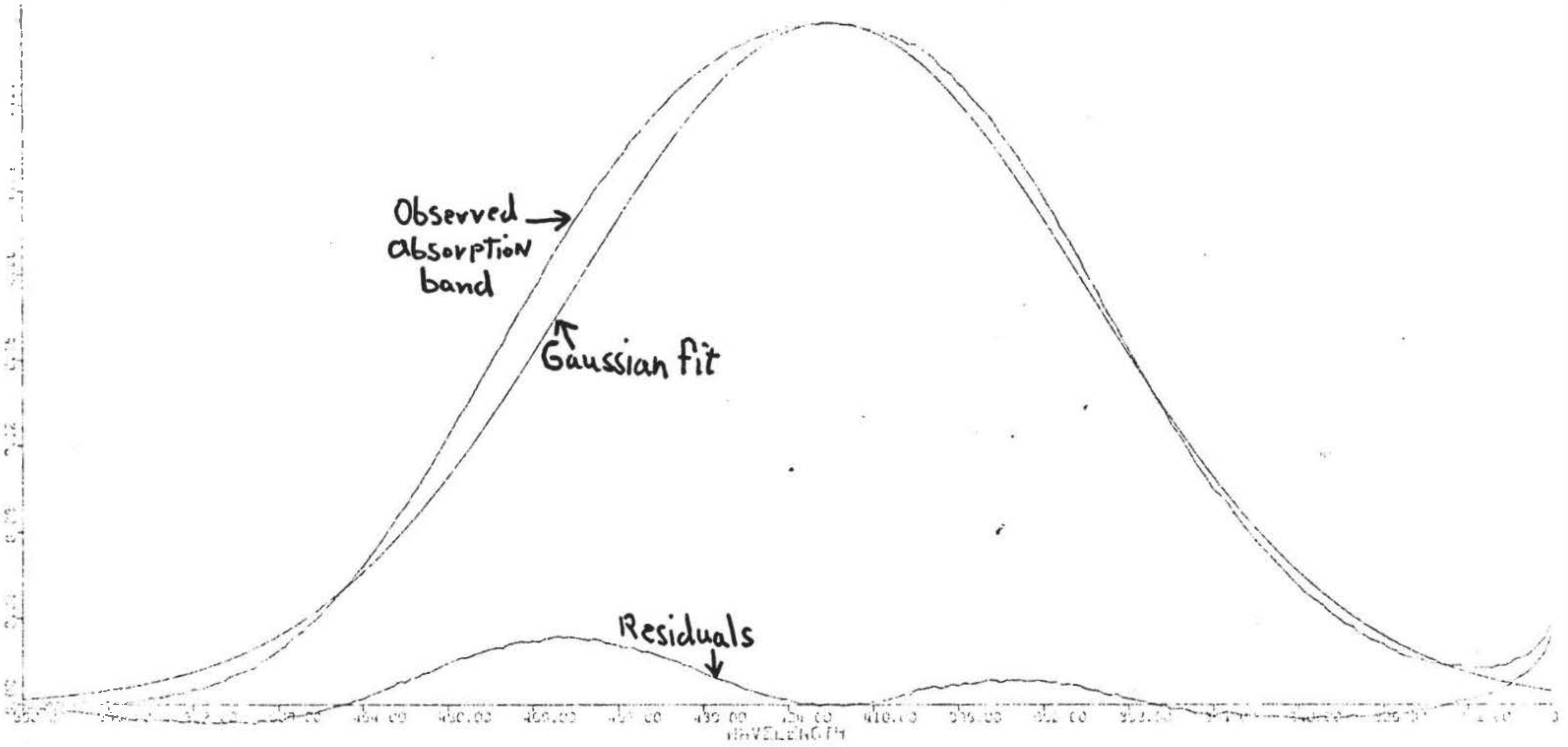
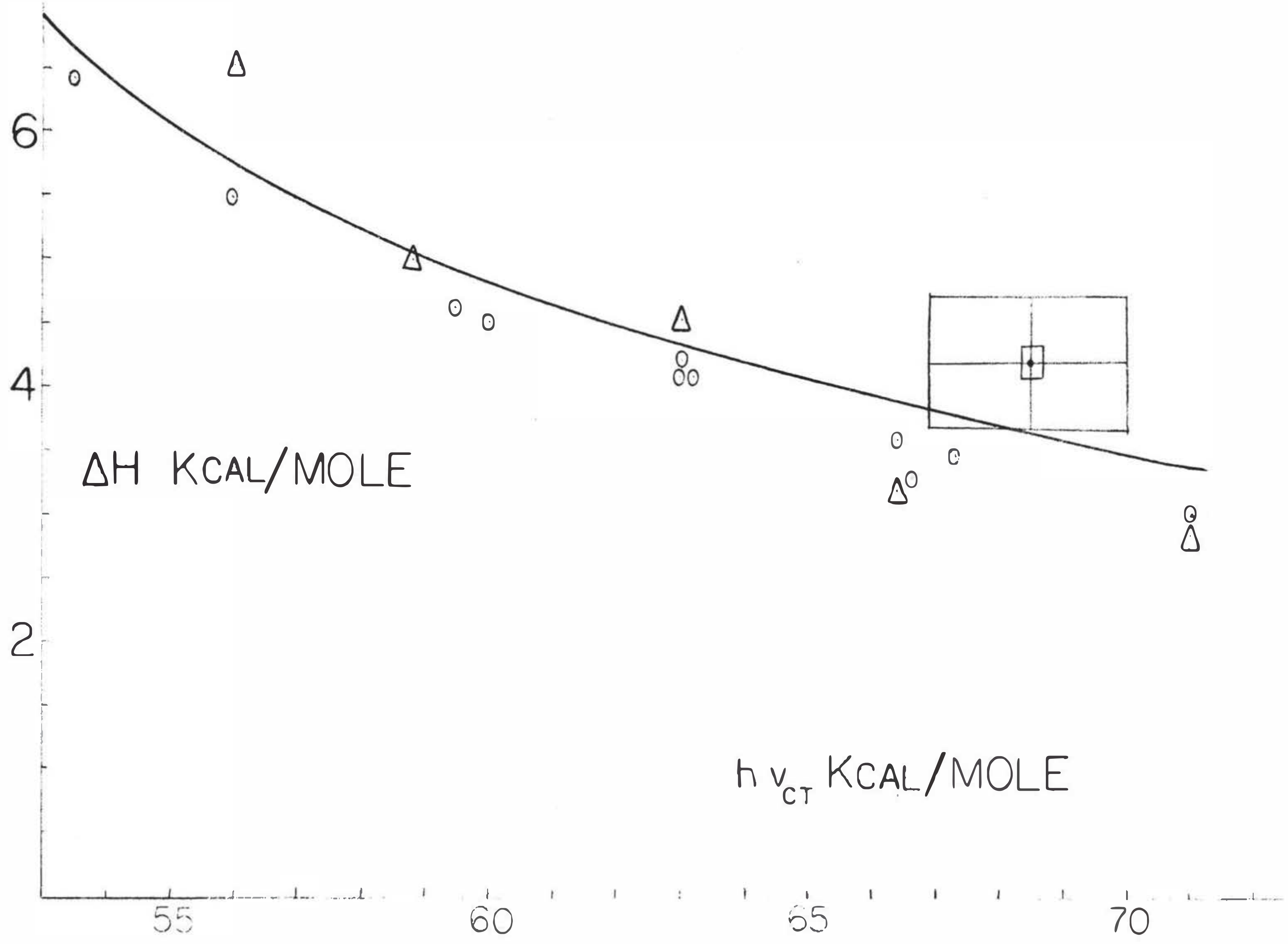

Observed absorption band
Gaussian fit
Residuals
494.00
480.00
466.00
452.00
438.00
424.00
410.00
396.00
382.00
368.00
WAVELENGTH

Figure 22

Graph of theoretical relationship between ΔH and $h\nu_{ct}$ prepared from empirical parameters along with the data of Chan and Laio, and the data of Merrifield and Phillips. The values for TBB/TCNE complex appear along with error bars for the uncertainty in ΔH and $h\nu$. The uncertainty in ΔH was evaluated from slope analysis of the plot of ln(K) versus 1/T.


6
4
2
ΔH KCAL/MOLE
55
60
65
70
h v_{CT} KCAL/MOLE

However difficulties were encountered in the dipole measurements of the complex (μ_h). Initially measurements were to be taken in a tertiary system with CCl_4 as solvent; however the small amount of complex formed in these solutions prevented these measurements. TCNE was then dissolved in pure t-butylbenzene yielding a saturated solution of approximately only .005 mole fraction. Although dipole determinations are usually made with solution concentrations in the range of .0 to .1 mole fraction, dielectric measurements were attempted. A linear plot of density versus mole fraction was obtained. However, the observed dielectric constants departed sporadically from the anticipated linear variation with mole fraction. It was concluded that the concentration of these solutions were approximately an order of magnitude too small for reliable dielectric measurements. In addition, it was noted that at these very high sensitivities, the measurements were extremely susceptible to trace impurities.

In conclusion, the thermodynamic and spectral properties of the t-butylbenzene/TCNE molecular complex have been measured for the first time and, within experimental uncertainties, have been found to be mutally compatible with the Mulliken charge transfer parameters that describe the methylated benzene/TCNE series. This result suggests that the steric properties of the t-butyl group do not significantly affect the bond strength or excited state energy of this complex. A relationship between the heat of formation and the charge transfer dipole has been derived. Since the steric properties of t-butylbenzene do not significantly affect the charge transfer bond energy, then it may be reasonible to assume that the contribution of the dative sturcture to the dipole moment is similarly unaffected.

Then the charge transfer dipole moment can be predicted from the correlation of ΔH with μ_{ct} and a knowledge of the heat of formation. However experimental difficulties precluded the verification of this predicted dipole moment.

APPENDIX 1

Dipole Theory[d]

A molecule exhibits a dipole moment if its center of charge does not correspond with its center of mass. The dipole moment is defined mathematically as $\vec{\mu} = \vec{r} \cdot q$ where r is the separation and q is the charge separated. In addition to a permanent dipole , molecules can exhibit an induced dipole due to distortion of the electronic configuration. This is termed distortion polarization. The vector resultant of the induced and permanent dipoles per volume is called the total polarization, $\vec{P}$.

(1) $\vec{P} = \vec{M}N_0/\bar{V} = (\rho/M)\ N_0\vec{M}$

where $\vec{M}$ is the total dipole moment in an applied field, $\bar{V}$ is the molar volume, N_0 is Avagadro's number, ρ is the density, and M is the molecular weight.

If a capacitor in a vacuum has a capacitance C_0 and upon addition of a dielectric media to produce a new capacitance C, then the dielectric constant (ε) is defined by: $\varepsilon = C/C_0 > 1$ the dielectric constant is also given by:

(2) $\varepsilon = \vec{E}_a + 4\pi\vec{P}/\vec{E}_a$

where $\vec{E}_a$ is the applied field. The average dipole moment is given by:

(3) $\vec{M} = \alpha\vec{F}$

where α is the polarizability and $\vec{F}$ is the local field intensity.

(4) $\vec{F} = \vec{E} + 4/3\pi\vec{P}$

Solving equations (1), (2), (3) and (4) simultaneously yields the following equation known as the Clausius-Mosetti equation.

(5) $$\frac{\varepsilon - 1}{\varepsilon + 2}\,\frac{m}{\rho} = \frac{4\pi}{3}N_0\alpha = P_m$$

---

[d] from lecture by Dr. Giles Henderson.

Where α is considered to consist of a distortion polarizability (α_o) and an orientation polarizability (α_μ) and Pm is known as the molar polarization.

The tendency of the dipole moment to orient itself with the applied field is opposed by thermal effects. The component of the dipole moment oriented with the field is given by $\mu\cos\theta$ where θ is the angle μ makes with the applied field. The distribution of orientations with the field must be accessed in order to obtain the average dipole in the field direction. The potential energy of a molecule as a function of θ is given by:

$$V_{(\theta)} = -\vec{\mu}\cos\theta \times \vec{F}$$

The average dipole in the direction of the field is given by:

$$\langle m\mu \rangle = (\mu_z N_z)_{avg}$$

Where N_z is the number of molecules with component μ_z.

Assuming a boltzman distribution:

$$\langle m_\mu \rangle = (\mu\cos\theta)\, e^{(\mu\cos\theta\vec{F}/kt)}{}_{avg}$$

In general $V(\theta)$ is much less than kt; and therefore, the following approximation can be made.

$$e^x \approx 1 + x + x^2/2 \cdots \approx 1 + x$$

$$\therefore \langle m\mu \rangle = \left[\mu\cos\theta\left(1 + \frac{\vec{F}\mu\cos\theta}{kt}\right)\right]_{avg.}$$

$$= \mu^2 \frac{\vec{F}}{kt} \frac{\int_0^{2\pi} \cos^2\theta\, d\omega}{\int_0^{2\pi} d\omega} = \frac{\mu^2\vec{F}}{3kt}$$

from equation (3): $\vec{m} = \alpha\vec{F} = \alpha\mu\vec{F} + \alpha_o\vec{F}$

$$\therefore \langle m\mu \rangle = \frac{\mu^2\vec{F}}{3kt} = \alpha\mu\vec{F}$$

$$\therefore (6)\ \alpha\mu = \frac{\mu^2}{3kt}$$

Where $\alpha\mu$ is the orientation polarizability.

Recalling equation (5):

$$(5)\quad \frac{\varepsilon-1}{\varepsilon+2}\,\frac{m}{\rho} \equiv P_m = \frac{4\pi}{3}N_0\left(\alpha_\mu+\alpha_0\right) = \frac{4\pi N_0}{3}\left(\frac{\mu^2}{3kT}+\alpha_0\right)$$

$$\therefore (7)\quad P_m = \frac{4\pi N_0\mu^2}{3K}\left(1/T\right) + \frac{4\pi N_0\alpha_0}{3}$$

The first term is referred to as the orientation polarization and the second as the distortion polarization. When measuring dipole moments an alterating field is generally used. Equation (7) is valid providing frequencies are low enough to allow the molecule to orient itself. This occurs in the radio frequency range. At optical frequencies the molecule can no longer orient itself and the polarization is due entirely to distortion polarization since electronic motions are very rapid. At optical frequencies: $\varepsilon = n^2$ where n^2 is the square of the index of refraction. Therefore equation (5) becomes:

$$\frac{n^2-1}{n^2+2}\,\frac{m}{\rho} \equiv P_m \equiv P_d = \frac{4\pi}{3}N_0\alpha_0$$

Where Pd is the distortion polarization. Therefore if ε and n can be measured, μ can be calculated from equation (7). However ε is not measured directly because of dipole-dipole interactions in the undiluted material. In general, gas or solution measurements are made where the solute is surrounded by a nonpolar solvent preventing solute-solute interactions.

For solutions:

$$P_{12m} = X_1P_{1m} + X_2P_{2m} = \frac{\varepsilon_{12}-1}{\varepsilon_{12}+2}\left(\frac{X_1m_1+X_2m_2}{\rho_{12}}\right)$$

Where subscripts 1 and 2 refer to properties of solvent and solute respectively, 12 refer to solution properties, and x refers to mole fraction.

Since the solvent is nonpolar:

$$P_{1m} = \frac{n_1^2-1}{n_1^2+2}\ \frac{m_1}{e_1}$$

$$\therefore (8)\ P_{2m} = \frac{1}{x_2}\left[\frac{\varepsilon_{12}-1}{\varepsilon_{12}+2}\ \frac{(x_1 m_1 + x_2 m_2)}{\rho_{12}} - \left(\frac{n_1^2-1}{n_1^2+2}\right)\frac{m_1 x_1}{e_1}\right.$$

To use this equation, P_{2m} for several concentrations must be measured and extrapolated to infinite dilutions. In practice the method Headstrand is easier to apply. Substituting the following empirical relationships into equation (8) obtains equation (9).

$$\varepsilon_{12} = \varepsilon_1 + a x_2$$
$$e_{12} = e_1 + b x_2$$

$$(9)\ P_{2m} = \frac{3 m_1 a}{(\varepsilon+2)^2 e_1} + \frac{\varepsilon_1 - 1}{(\varepsilon+2) e_1}\left(m_2 - \frac{m_1 b}{e_1}\right)$$

Therefore if a and b can be determined from linear plots of ε_{12} versus x_2 and ρ_{12} versus x_2, then P_{2m} can be calculated. $P_{2\mu}$ can be evaluated from the index of refraction:

$$P_{2\mu} = P_{2m} - P_{2d} = P_{2m} - \frac{n_2^2-1}{n_2^2+2}\ \frac{m_2}{e_2}$$

Finally, the dipole moment can be calculated from :

$$P_{2\mu} = \frac{4\pi N_0}{3}\left(\frac{\mu^2}{3Kt}\right)$$

APPENDIX 2

Development of Benesi-Hildebrand Equation[e]

The equilibrium constant for complex formation is given by: (t-butylbenzene) + (TCNE) $\rightleftharpoons$ (CT)

(1) Keq = (CT)/(TBB)(TCNE)

Where the parenthesis refer to molar concentrations.

The concentration of the complex is (CT) = A/εl

Where A is the absorption, ε is the molar extinction coefficient, and l is the path length. If measurements are made in excess t-butylbenzene, then $(TBB)^{o} \cong (TBB)$ and $(TCNE) = (TCNE)^{o} - (CT)$.

Substituting into equation (1):

$$K = \frac{A}{\varepsilon l([TCNE]^{\circ}[TBB]^{\circ} - A[TBB]^{\circ}}$$

Rearranging:

$$1/K = \frac{\varepsilon l([TCNE]^{\circ}[TBB]^{\circ} - A[TBB]^{\circ}}{A}$$

$$\therefore \frac{\varepsilon l[TCNE]^{\circ}[TBB]^{\circ}}{A} = \frac{1}{K} + [TBB]^{\circ}$$

Finally:

$$\frac{[TCNE]^{\circ}[TBB]^{\circ}}{A} = \frac{1}{\varepsilon l K} + \frac{[tBB]^{\circ}}{\varepsilon l}$$

If a plot is made of the left hand side versus $(TBB)^{o}$, a linear graph is obtained with a slope of 1/εl and an intercept of 1/εlk. K is evaluated as slope over intercept and εl is evaluated as one over the intercept.

---

e from lecture by Dr. Giles Henderson

o refers to concentration prior to equilibrium

APPENDIX 3

Research Programs

```
$JOB              112DCN MUNDELL      CHM
      DIMENSION X(100),Y(100),E(100),P(100),XI(100)
      COMMON AM,AB,SIGMA
      N = 5
      READ(5,30) (X(I),I = 1,N)
   30 FORMAT(7(F10.2))
      READ(5,80) (P(I),I = 1,N)
   80 FORMAT(7(F10.7))
      READ(5,90) (XI(I),I = 1,N)
   90 FORMAT(7(F10.9))
      READ(5,400)ANT,PT,AMT,PC,EC,CM
  400 FORMAT(6(F10.5))
      WRITE(6,60)
   60 FORMAT(1H ,8X,'THE DIAL SETTING',3X,'THE DIELECTRIC CONSTANT')
      READ(5,40) (E(I),I = 1,N)
   40 FORMAT(6(F10.5))
      WRITE(6,70) (X(I),E(I),I = 1,N)
   70 FORMAT(1H ,10X,F10.2,5X,F10.7)
      CALL RAZZ(N,XI,P)
      BB = AM
      WRITE(6,200) BB,AB,SIGMA
  200 FORMAT(1H1,'B = ',F10.5,//,' DENSITY CCL4 = ',F10.5,//,' STANDARD
     ADEVIATION = ',F10.5)
      CALL RAZZ(N,XI,E)
      AA = AM
      WRITE(6,300) AM,AB,SIGMA
  300 FORMAT(1H ,'A = ',F10.5,//,' DIELECTRIC CONSTANT CCL4 = ',F10.5,
     B//,' STANDARD DEVIATION = ',F10.5)
      XC = EC + 2.
      YC = (EC - 1.)/(XC*PC)
      XCT = (XC**2)*PC
      ZK = 1.38054E-16
      PI = 3.1415926535
      AN = 6.023E23
      T = 298.12
      PM = 3.*CM*AA/XCT + YC*(AMT-CM*BB/PC)
      RM = (((ANT**2)-1.)/((ANT**2)+2.))*(AMT/PT)
      PU = PM - RM
      XU = 9.*PU*ZK*T*1.E36
      FU = 4.*PI*AN
      XU = SQRT(XU/FU)
      WRITE(6,500)PM,RM,PU,XU
  500 FORMAT(1H0,' MOLAR POLARIZATION = ',F10.5,//,' DISTORTION POLARIZA
     CTION = ',F10.5,//,' ORIENTION POLARIZATION = ',F10.5,//,' DIPOLE
     DMOMENT = ',F12.8)
      RETURN
      END

      SUBROUTINE RAZZ(N,X,Y)
      DIMENSION X(100),Y(100),RI(100)
      COMMON AB,AM,SIGMA
      SUMX = 0
       SUMY = 0
       SUMXSQ = 0
       SUMXY = 0
      DO 4 I = 1,N
       SUMX = SUMX + X(I)
       SUMY = SUMY + Y(I)
       SUMXSQ = SUMXSQ + X(I)*X(I)
       SUMXY = SUMXY + X(I)*Y(I)
```

```
SUBROUTINE RAZZ          73/72    OPT=1

                         SUBROUTINE RAZZ(N.X.Y)
                         DIMENSION X(100).Y(100),RI(100)
                         COMMON AB.AM.SIGMA
                         SUMX = 0
                          SUMY = 0
                          SUMXSQ = 0
                          SUMXY = 0
                         DO 4 I = 1.N
                          SUMX = SUMX + X(I)
                          SUMY = SUMY + Y(I)
                          SUMXSQ = SUMXSQ + X(I)*X(I)
                          SUMXY = SUMXY + X(I)*Y(I)
                     4    CONTINUE
                          EN = N
                          DEN = EN*SUMXSQ - SUMX*SUMX
                         AM = (SUMXY*EN - SUMX*SUMY)/DEN
                         AB = (SUMXSQ*SUMY - SUMX*SUMXY)/DEN
                          SUMRSQ = 0
                          DO 5 I = 1,N
                         RI(I) = Y(I)- AM*X(I) - AB
                     5    SUMRSQ = SUMRSQ + RI(I)*RI(I)
                         CI = N
                         SIGMA =  SQRT(SUMRSQ/CI)
                         RETURN
                          END


         SYMBOLIC REFERENCE MAP (R=1)

    ENTRY POINTS
       3   RAZZ

    VARIABLES       SN   TYPE                 RELOCATION
       0   AB           REAL                    / /                1   AM
      66   CI           REAL                                      64   DEN
      63   EN           REAL                                      62   I
       0   N            INTEGER                   F.P.            67   RI
       2   SIGMA        REAL                    / /               65   SUMR
      56   SUMX         REAL                                      60   SUMX
      51   SUMXY        REAL                                      57   SUMY
       0   X            REAL          ARRAY       F.P.             0   Y

    EXTERNALS            TYPE     ARGS
           SQRT         REAL        1 LIBRARY

    STATEMENT LABELS
       0   4                                                 0   5

    LOOPS   LABEL      INDEX       FROM-TO      LENGTH      PROPERTIES
      14    4          I              8 13         10B          OPT
      43    5          I             19 21          6B          OPT
```

```
    4    CONTINUE
         EN = N
         DEN = EN*SUMXSQ - SUMX*SUMX
         AB = (SUMXY*EN - SUMX*SUMY)/DEN
         AM = (SUMXSQ*SUMY - SUMX*SUMXY)/DEN
         SUMRSQ = 0
         DO 5 I = 1,N
        RI(I) = Y(I)- AM*X(I) - AB
    5    SUMRSQ = SUMRSQ + RI(I)*RI(I)
        CI = N
        SIGMA = SQRT(SUMRSQ/CI)
        RETURN
         END
```

```
   $ENTRY
  THE DIAL SETTING.   THE DIELECTRIC CONSTANT
         464.00        2.2347000
         511.00        2.2334990
         602.00        2.2460000
         658.00        2.2505990
         755.00        2.2585000
```

```
B =    -1.03417

DENSITY CCL4 =     1.57654

STANDARD DEVIATION =     2.39163
A =      2.20056

DIELECTRIC CONSTANT CCL4 =     2.22863

STANDARD DEVIATION =     1.26780
```

```
B =    -1.03417

DENSITY CCL4 =      1.57654

STANDARD DEVIATION =      2.39163
A =      0.20056

DIELECTRIC CONSTANT CCL4 =      2.22863

STANDARD DEVIATION =      1.85789

 MOLAR POLARIZATION =    46.27876

DISTORTION POLARIZATION =     45.01648

ORIENTION POLARIZATION =      1.26228

DIPOLE  MOMENT =    0.24854680

CORE USAGE          OBJECT CODE=      3936 BYTES,ARRAY AREA=      2412 BYTES,TOT

DIAGNOSTICS           NUMBER OF ERRORS=          0, NUMBER OF WARNINGS=        C

COMPILE TIME=       1.96 SEC,EXECUTION TIME=       0.44 SEC,  WATFIV - VERSIC
```

Program for Calculation of the Equilibrium Constant and Molar Extinction Coefficient by The Benesi-Hildebrand Equation

Input

Z(M) & P(I) = ((TCNE)(TMB)/absorption) of solutions

X(I) = TMB molarities of solutions

N = Number of points

T(I) = Temperatures of absorption measurements

Output

XK = Equilibrium constant

AB = Slope of Benesi-Hildebrand plot

AM = Intercept of Benesi-Hildebrand plot

SUBROUTINE RAZZ is a linear least squares program.

```
      PROGRAM ZAZZZ(INPUT.OUTPUT,TAPE5=INPUT.TAPE6=OUTPUT)
      DIMENSION V(50)
      DIMENSION T(50)
      DIMENSION P(50).X(50).Z(50)
      DIMENSION XK(50)
      DIMENSION Y(50)
      COMMON AB,AM.SIGMA
      N = 5
      READ(5.30) (P(I).I = 1,N)
 30   FORMAT(6E10.4)
      READ(5.40) (X(I),I = 1,N)
  40  FORMAT(6F8.5)
 25   CALL RAZZ (N,X,P)
      XK(1) = AM/AB
      WRITE(6.300) AB,AM,SIGMA
 300  FORMAT(1H .'SLOPE = '.E10.4.'INTERCEPT = '.E10.4.'SIGMA = 'E10.4)
      WRITE(6.400) XK(1)
 400  FORMAT(1H .'EQUALIBRIUM CONSTANT = '.F10.5)
      T(1) = 6.2
      T(2) = 26.9
      T(3) =34.7
      T(4) = 44.3
      T(5) = 54.8
      T(6) = 64.4
      DO 50 J = 1,6
      W = 1.58439 + 1.925E-3 * (24.8 - T(J))
      W = W/1.58439
      READ(5.60) (Z(M). M = 1.5)
  60  FORMAT(5E10.4)
      DO 10 I = 1.5
      P(I) = Z(I)
      V(I) = X(I)*W
 10   CONTINUE
      CALL RAZZ(N.V.P)
      XK(L) = AM/AB
      WRITE(6.350) AB.AM.SIGMA
 350  FORMAT(1H .'SLOPE = '.E10.4,'INTERCEPT = '.E10.4,'SIGMA = 'E10.4)
      WRITE(6.450) XK(L)
 450  FORMAT(1H .'EQUALIBRIUM CONSTANT = ',F10.5)
 50   CONTINUE
      CALL EXIT
      END
```

```
C REFERENCE MAP (R=1)


SN   TYPE                 RELOCATION
   REAL                       / /                   1   AM        REAL                       / /
   INTEGER                                       4334   J         INTEGER
   INTEGER    *UNDEF                             4336   M         INTEGER
   INTEGER                                       4504   P         REAL         ARRAY
```

Program for Calculation
Of the Heat of Formation

Input

R = Gas constant

X(I) = Temperatures of measurements

Y(I) = Equilibrium constants

Output

H = Heat of formation

SUBROUTINE RAZZ is a linear least squares program.

```
7A777         73/72    OPT=1                                        FTN 4.5+410             76/0

       PROGRAM 7A777(INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)
        DIMENSION X(50),Y(50)
       COMMON AB,AM,SIGMA
       R = 1.9872
       READ(5,10) (X(I), I = 1,7)
 10     FORMAT(7F6.1)
       READ(5,20) (Y(I), I = 1,7)
 20     FORMAT(7F8.5)
       DO 30 I = 1,7
       X(I) = 1.0/(X(I) +  273.14)
       Y(I) = ALOG(Y(I))
 30    CONTINUE
       N = 7
       CALL RA77 (N,X,Y)
       H = R*AM
       S = R*AB
       WRITE(6,555) H,S
 555   FORMAT(1H ,*HEAT OF FORMATION = *,F10.5,*  S = *,F10.5)
       CALL EXIT
       END


FERENCE MAP (R=1)


TYPE              RELOCATION
EAL                   / /                       1  AM          REAL                        / /
EAL                                          4202  I           INTEGER
NTEGER                                       4201  R           REAL
EAL                                             2  SIGMA       REAL                        / /
EAL          ARRAY                           4270  Y           REAL          ARRAY

MODE
               2041  OUTPUT                              0  TAPE5          FMT                   2

 TYPE      ARGS
EAL          1 LIBRARY                         EXIT                       0
             3


                         4161   20          FMT                                             0  30

DEX        FROM-TO     LENGTH     PROPERTIES
             9  12        78                  EXT REFS

NGTH
    3

                RA78       167
                4103       2117
```

Program for Gaussian Fit of the Charge Transfer Absorption Band

Input

AO = Maximum absorption for CT band

XO = λmax for CT band

XH = λmax at half AO

X(I) = Wavelength

A(I) = Absorption

Output

A = CT band

GA = Gaussian Fit

P = Residuals

AXIS = Program for plotting the axis.

LINE = Program for plotting the points.

```
FORTRAN IV G LEVEL  21                  MAIN                DATE = 76205            20/28/55

              DIMENSION IBUF(1000)
              DIMENSION W(255),A(255),GA(255),X(255),R(255)
              READ (5,10) (W(I),A(I), I = 1,253)
        10    FORMAT(F4.0,F5.3)
              AO = 0.318
              WO = 417.0
              XH = 50.0
              SIGMA = XH**2/(2.0*ALOG(2.0))
              DO 20 I = 1,253
              X(I) = W(I)-WO
              AG = -1.0*X(I)**2/(2.0*SIGMA)
              GA(I) = AO*EXP(AG)
              R(I) = A(I) - GA(I)
        20    CONTINUE
              W(254) = 550
              W(255) = -14.0
              A(254) = 0.0
              A(255) = 0.04
              GA(254) = 0.0
              GA(255) = 0.04
              R(254) = 0.0
              R(255) = 0.04
              CALL INIT
              FACT = 10.0/18.0
              CALL PLOT (1.0,1,0,-3)
              CALL FACTOR(FACT)
              CALL AXIS (0.0,0.0,10HABSORBTION,+10,9.0,90.0,A(254),A(255))
              CALL AXIS(0.0,0.0,10HWAVELENGTH.-10,18.0,0.0,W(254),W(255))
              CALL LINE(W,A.253,1,0,0)
              CALL LINE(W,GA,253,1,0,0)
              CALL LINE(W,R,253,1,0,0)
              CALL PLOT(14.0,0.0,999)
              STOP
              END
```

APPENDIX L

Derivation of Equation XV

From I:

$$(1)\quad -b/a = \frac{W_c - W_n}{H_{o1} - W_nS} \quad \text{or} \quad b = -a\,\frac{W_o - W_n}{H_{o1} - W_nS} \quad \text{or} \quad a = -b\,\frac{(H_{c1} - W_nS)}{(W_c - W_n)}$$

Substituting (1) in for b in the normalization constraint ($a^2 + b^2 + 2abS = 1$)

$$a^2 + \frac{(W_o - W_n)^2}{(H_{o1} - W_nS)^2}\,a^2 - 2S\,\frac{W_o - W_n}{H_{o1} - W_nS}\,a^2 = 1$$

Rearranging:

$$(2)\quad a^2 = \frac{1}{1 + \frac{(W_c - W_n)^2}{(H_{o1} - W_nS)^2} - \frac{2S(W_c - W_n)}{H_{c1} - W_n S}} = \frac{(H_{c1} - W_nS)^2}{DEN}$$

where $DEN = (H_{o1} - W_nS)^2 + (W_o - W_n)^2 - (W_o - W_n)(H_{o1} - W_nS)2S$

Employing the same method to solve for b^2:

$$b^2 + \left[\frac{(H_{o1} - W_nS)}{(W_c - W_n)}\right]^2 b^2 - 2S\,\frac{(H_{c1} - W_nS)}{(W_o - W_n)}\,b^2 = 1$$

$$(3)\quad b^2 = \frac{1}{1 + \left(\frac{H_{c1} - W_nS}{W_b - W_n}\right)^2 - 2S\,\frac{(H_{o1} - W_nS)}{(W_b - W_n)}} = \frac{(W_b - W_n)^2}{DEN}$$

Rearranging the normalization constraint and substituting for b^2 & a^2 with Equation 2 and Equation 3:

$$ab = \frac{1 - a^2 - b^2}{2S} = \frac{1 - \frac{(W_b - W_n)^2}{DEN} - \frac{(H_{c1} - W_nS)^2}{DEN}}{2S}$$

$$\therefore (4)\quad ab = \frac{DEN - (W_o - W_n)^2 - (H_{o1} - W_n S)^2}{2S\ DEN}$$

From (3) & (4)

$$\therefore\ b^2 + abs = \frac{(W_o - W_n)^2}{DEN} + S\left[\frac{DEN - (W_o W_n)^2 - (H_{o1} - W_n S)^2}{2S\ DEN}\right]$$

$$= \frac{(W_o - W_n)^2 - \tfrac{1}{2}(W_o - W_n)(H_{o1} - W_n S)\, 2S}{DEN}$$

where $B_n = H_{o1} - W_n S$

$$= \frac{(W_o - W_n)^2 - (W_o - W_n)\, B_n S}{(W_o - W_n)^2 + B_n^2 - 2S(W_o - W_n) B_n}$$

Since $W_n \cong \Delta H$ an $\mu_{ct} = (b^2 + abs)\,\mu_1$

$$\mu_{ct} = \left[\frac{(W_o - \Delta H)^2 - (W_o - \Delta H)\, B_n S}{(W_o - \Delta H)^2 + B_n^2 - 2S\, B_n (W_o - \Delta H)}\right]\mu_1$$

$$\therefore\ \mu_{ct} = \left[\frac{W_o - \Delta H - B_n S}{W_o - \Delta H + B_n^2/(W_o - \Delta H) - 2S\, B_n}\right]\mu_1$$

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