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QUANTITATIVE INFRARED SPECTROPHOTOMETRY OF ORGANIC NITRATE ESTERS

Yvon P. Carignan, et al

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May 1972

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QUANTITATIVE INFRARED SPECTROPHOTOMETRY OF ORGANIC NITRATE ESTERS

BY
YVON P. CARIGNAN
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MAY 1972

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A quantitative infrared analysis of the N = O asymmetric stretching vibration band for the nitrate esters, ethyl nitrate, amyl nitrate, ethylene glycol dinitrate, glycerol trinitrate, and cellulose nitrate (12.53% N) is presented. Two solvents, chloroform and tetrahydrofuran were used; in both cases the validity of Beer's law appears well established over a reasonable range of concentration and cell path length.

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Propellants Division
Feltman Research Laboratory
Picatinny Arsenal
Dover, New Jersey

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ACKNOWLEDGEMENT

We acknowledge the valuable assistance of Mr. N. Gelber in the determination of the nitrogen content of the nitrate esters used in this study.

ABSTRACT

A quantitative infrared analysis of the N=O asymmetric stretching vibration band for the nitrate esters, ethyl nitrate, amyl nitrate, ethylene glycol dinitrate, glycerol trinitrate, and cellulose nitrate (12.53%) is presented. Two solvents, chloroform and tetrahydrofuran were used; in both cases the validity of Beer's law appears well established over a reasonable range of concentration and cell path length.

CONCLUSION

For the five nitrate esters studied, Beer's law for the absorbance of the N=O asymmetric stretching band is found to be generally obeyed. In other words, from a measure of the absorbance one could calculate the amount of a given nitrate ester present in solution. The low absorptivity <u>a</u> for cellulose nitrate deserves some comment. The band shape for cellulose nitrate is significantly broader and consequently measurement of the absorbance at the band maximum is not a true indication of the absorption intensity. A more realistic measurement would be the integrated intensity of the band.

RECOMMENDATION

It is recommended that this study be extended to a number of cellulose nitrates covering a wide range in nitrogen content. An important point to establish is whether the absorptivity <u>a</u> for the N=O asymmetric stretching vibration is a constant or a function of the nitrogen content.

INTRODUCTION

Organic nitrate esters are the most prominent ingredients in solid propellant formulations. Among the most commonly known esters of this type are glycerol trinitrate (nitroglycerin), cellulose nitrate (nitrocellulose), ethylene glycol dinitrate, butane triol trinitrate, and pentaerythritol tetranitrate. But the list of all organic nitrate esters evaluated to date in propellant formulations would probably not exceed a dozen or so compounds. This is far less than the known eight-hundred nitrate esters which form a distinct class of organic chemical compounds. It is thus realistic to anticipate that a large variety of nitrate ester compounds will be evaluated in future propellant formulations.

One important aspect of the chemistry and technology of nitrate esters is the number of analytical methods available for determining their purity. The nitrogen content, which reflects the substitution in nitrate groups, is usually determined by the DuPont nitrometer method (Ref. 1) or by titration (Refs 2 and 3). Both of these methods are well established and of sufficient accuracy. They have, however, shortcomings in terms of convenience of manipulation, time of handling and quantity of sample required per determination. A third method of analysis, the well-known micro Dumas, would require only a few milligrams of sample per determination. Unfortunately, this method does not appear to be applicable to the polynitrate esters, for which titration usually gives low nitrogen values (Ref. 4). Quite recently a microscopic method based on dispersion staining (Ref. 5) has been developed for determining the degree of nitration of cellulose nitrate. For cellulose nitrates ranging in nitrogen content from 12.55 to 13.5%, agreement with the standard duPont nitrometer results was excellent. However, this microscopic method is strictly limited to cellulose nitrate. A modified version of the microscopic method has been suggested for inclusion in military specifications (Ref. 6). It is our opinion that, although this method based on refractive index measurement is extremely simple and fast, it lacks in scope and can only be used for cellulose nitrates of limited range in nitrogen content.

Polarography has also been considered as a potential analytical tool for the study of nitrate esters. In principle, this technique offers very attractive features, one being the small amount of sample required. But, so far, this technique has not proven too successful as a quantitative tool for a number of nitrate esters. In the case of cellulose nitrate for example, no diffusion current is detectable because of the extremely slow diffusion of the polymer at the dropping mercury electrode. Also, nitrate esters with any degree of volatility would not be amenable to precise quantitative study by this technique because of evaporation losses which may occur under the flow of nitrogen during the deoxygenation step.

One analytical technique for nitrogen determination of nitrate esters which promises to be of wide scope is infrared spectrophotometry. This technique offers a number of interesting features: (a) it is non-destructive and safe to carry out, (b) the technique can be developed to handle samples as small as ten milligrams, and (c) it is applicable to cellulose nitrate as well as to highly volatile nitrate esters. The limited work already reported in the literature (Ref. 7 and 8) indicates that this spectroscopic technique could be made competitive in terms of accuracy and reproducibility with the best conventional methods. But most important is the realization that the infrared procedure is far superior to the other methods in terms of ease and convenience of operation and scope of application.

The work described in the present report represents an attempt to establish the scope and applicability of the infrared technique for a variety of nitrate esters. The actual procedure used differs from previous ones in that a variable path length cell is used for infrared measurements.

RESULTS AND DISCUSSION

The precision and accuracy of the micrometer scale of the variable path length cell were determined by the method of interference fringes. The true path length between the windows was calculated in accordance with the formula

$$b = \frac{n}{2(\lambda 2 - \lambda 1)} \qquad (1)$$

where b = path length in cm
n = number of fringes between starting and finishing frequency (cm^{-1})
$\lambda 2$ = starting frequency (cm^{-1})
$\lambda 1$ = finishing frequency (cm^{-1})

The calibration data is given in Table 1. It is observed that the deviations between the cell micrometer settings and the true path length decrease with an increase in path length, from 4.56% deviation at 70 microns path length to 0.92% deviation at 600 microns. Except for the longest path (600 microns), the reproducibility of the triplicate determinations is within one percent.

The analysis of the nitrate esters chosen for this study is based on the well-known fundamental Beer's law which relates the absorption at a particular wave length of radiation to the number and type of molecules. This law states that the absorbance (A) should be a linear function of the concentration of the absorbing material among other things. It is mathematically expressed as follows:

$$A = \log \left(\frac{I_0}{I}\right) = a \times b \times c \qquad (2)$$

where I_0 = incident radiation
I = transmitted radiation
a = absorptivity
b = sample thickness or internal cell length
c = concentration of the absorbing material
A = Absorbance

For measuring I_0 and I of the absorption bands, we have used the base line method.

In nitrate esters, the nitrate group gives rise to six active infrared absorption bands shown in Table 2. Of these, the most intense band is assigned to the N = 0 asymmetric stretching mode, and its high relative intensity makes this absorption particularly attractive for quantitative study. However, this band falls in the 1620 - 1680 cm^{-1} spectral region, where atmospheric water also absorbs. Even with double beam spectrometers, this moisture absorption is never completely eliminated. To reduce atmospheric absorption to a minimum, all measurements were done under a dry air purge.

Our study embraces five different nitrate esters: ethyl nitrate, amyl nitrate, ethylene glycol dinitrate, glycerol trinitrate, and cellulose nitrate. Their chemical compositions are shown in Table 3. Two solvents, chloroform and tetrahydrofuran, which are transparent in the spectral region of interest, were used to prepare the solutions. The shapes of the absorption bands of the individual nitrate esters are reproduced in Figures 1 through 5. All the bands were found to be narrow with a half-band width of the order of 25 cm^{-1}. With ethylene glycol dinitrate, there is some evidence of a close doublet at the maximum of the band. The band shape for cellulose nitrate appears less symmetrical, presumably because the monomeric units have their nitrate groups distributed in three chemically different patterns.

<u>Ethyl Nitrate</u>

Tables 4 - 5
Figures 6 - 7

The straight line relationship found establishes the validity of Beer's law for this molecule. The average absorptivity constant, $\underline{a}$, is calculated to be 7.23×10^5 cm^2, $mole^{-1}$. There is indication that $\underline{a}$ may be slightly higher in tetrahydrofuran.

<u>Amyl Nitrate</u>

Tables 6 - 8
Figures 8 - 10

In general, Beer's law is obeyed for this molecule also. In chloroform, $\underline{a}$ takes an average value of 7.88×10^5 cm^2 $mole^{-1}$ while in tetrahydrofuran the value is 8.66×10^5 cm^2, $mole^{-1}$.

<u>Ethylene Glycol Dinitrate</u>

Tables 9 - 12
Figures 11 - 14

In general, the plots of absorbance versus either path length or concentration show some curvature. This is confirmed by the $\underline{a}$ values which are found to decrease with concentration or path length by about 10%. In chloroform, the average $\underline{a}$ is 13.53×10^5 cm^2, $mole^{-1}$ as compared to 14.56×10^5 cm^2, $mole^{-1}$ found in tetrahydrofuran. Since this molecule contains two nitrate groups, $\underline{a}$ per nitrate group becomes 7.28×10^5 cm^2, $mole^{-1}$ (NO_2) in tetrahydrofuran and 6.77×10^5 cm^2, $mole^{-1}$ (NO_2) in chloroform.

Glycerol Trinitrate

Tables 13 - 16
Figures 15 - 18

The observations for glycerol trinitrate parallel those made for ethylene glycol dinitrate. However, the values for a are reversed in order. These values are found higher in chloroform, 22.24×10^5 $cm^2 \cdot mole^{-1}$ as compared to 19.40×10^5 $cm^2 \cdot mole^{-1}$ in tetrahydrofuran. Since this molecule contains three nitrate groups, a per nitrate group is calculated to be 7.41×10^5 $cm^2 \cdot mole^{-1}$ (NO_2) in chloroform and 6.47×10^5 $cm^2 \cdot mole^{-1}$ (NO_2) in tetrahydrofuran.

Cellulose Nitrate (12.53% N)

Tables 17 - 27
Figures 19 - 29

Because of a lack of solubility, no experiment could be conducted in chloroform. While it seems established by the results that Beer's law is obeyed reasonably well with this polymer in tetrahydrofuran, deviations from the straight line relationship appear to occur at path length settings greater than 400 microns. The average a values per nitrate group in the molecule for all experiments is 4.48×10^5 $cm^2 \cdot mole^{-1}$, a value substantially lower than those found in tests of the simpler nitrate ester.

EXPERIMENTAL PROCEDURES

Materials

Spectroscopic Solvents

Eastman-Kodak spectrograde chloroform and tetrahydrofuran were used as received.

Nitrate Esters

Ethyl nitrate white label was purchased from Eastman-Kodak. Attempt to establish its purity by the standard ferrous reduction method of the nitrate group yielded very low values. The average of triplicate determinations was 25.10% of theoretical. Evidently this analytical technique is unsatisfactory for volatile nitrate esters. The procedure was modified to prevent evaporation losses and, with this modification, the values were raised to 80% of theoretical.

Amyl nitrate was purchased from K & K Laboratories, Inc., Plainview, N. Y. The standard ferrous reduction method failed to yield acceptable results. The average of six determinations gave 56.6% of theoretical. However, modifications of the procedure to reduce evaporation losses was successful and the purity from triplicate determinations was shown to be higher than 99%. Ethylene glycol dinitrate was obtained from Trojan Powder Co., Allentown, Pennsylvania. Its purity, as determined by the ferrous reduction method was found to be 98.66% of theoretical.

Glycerol trinitrate was obtained from Hercules Powder Co., Kenvil, N. J. By the ferrous reduction method its purity was found to be 99.94% of theoretical.

Cellulose nitrate was supplied by Hercules Powder Co. Its nitrogen content, determined by the ferrous reduction method, was found to be 12.53%, which corresponds to a degree of substitution of 2.43.

Infrared Spectra

The infrared spectra were recorded on a Perkin-Elmer model 621 spectrophotometer. The following instrumental conditions were used

Slit program	1000 x 1
Gain	4 x 2
Attenuator speed	1100
Scan time	32

Suppression	6
Scale	IX
Source Current	0.8

The system was continuously purged with dry air in order to reduce the absorption arising from atmospheric moisture. A Perkin-Elmer variable path length cell was used for scanning the solutions.

Preparation of Solutions

The nitrate ester samples were weighed to the nearest 0.1 milligram in a 25 mil volumetric flask and the solvent was then added up to the calibrated mark. In the case of cellulose nitrate, the polymer was dried at 60°C for 3 hours under vacuum before weighing.

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Table 1 Calibration Data for the Variable Path Length Cell

Perkin-Elmer Cell No. 2004

b_I Microns	b_{t1}	b_{t2}	b_{t3}	b_I-b_{t1}	b_I-b_{t1}	b_I-b_{t3}	$\Delta\overline{b}$	$\bar{b}$	% Deviation
70	67.07	66.45	66.91	2.93	3.55	3.09	3.19	66.81	4.56
100	96.97	97.77	96.45	3.03	3.23	3.55	3.27	96.45	3.27
150	145.16	145.46	145.30	4.84	4.54	4.70	4.69	145.20	3.13
200	194.44	195.95	196.08	5.56	4.05	3.92	4.51	195.49	2.26
250	244.05	244.19	244.19	5.95	5.81	5.81	5.86	244.14	2.34
300	294.12	294.12	293.10	5.88	5.88	6.90	6.22	293.78	2.07
350	342.86	344.83	346.15	7.14	5.17	3.84	5.38	344.61	1.54
400	394.74	394.74	392.86	5.26	5.26	7.14	5.87	394.11	1.47
450	444.44	444.44	442.86	5.56	5.56	7.14	6.09	443.91	1.35
500	494.62	491.80	492.31	5.38	8.20	7.69	7.09	492.91	1.42
550	545.45	544.44	543.48	4.55	4.55	6.52	5.21	544.46	0.95
600	590.91	592.59	600.00	9.09	7.41	0.00	5.50	594.50	0.92

Micron = 0.0001 cm
b_I = Cell Micrometer Setting
b_t = Path length in microns by interference firings

$\overline{b}$ = Average deviation

$\bar{b}$ = Average path length in microns from interference firings measurements

Table 2 Characteristic Infrared Bands of the Nitrate Group

Band	Symbol	Assignment	Frequency Range (cm^{-1})	Relative Intensity
I	ν_a (NO_2)	Asym. N=O stretch	1680-1620	Very strong ε = 1500
II	ν_a (NO_2)	Sym. N=O stretch	1295-1265	Very strong ε = 1000
III	ν (ON)	O-N stretch	870-830	strong
IV	γ_w (NO_2)	out of plane	760-740	medium
V	δ (NO_2)	NO_2 bending	715-685	medium
VI	γ_r (NO_2)	in plane	555-577	weak

Table 3 Chemical Composition of Nitrate Esters

Ethyl Nitrate	$CH_3-CH_2-O-NO_2$ M. W. 91
Amyl Nitrate	$CH_3-CH_2-CH_2-CH_2-CH_2-O-NO_2$ M. W. 133
Ethylene Glycol Dinitrate	$O_2N-O-CH_2-CH_2-O-NO_2$ M. W. 227
Glycerol Trinitrate	$O_2N-O-CH_2-CH(NO_2)-CH_2-O-NO_2$ M. W. 227
Cellulose Nitrate (12.53% N)	$C_6H_7O_5\ (NO_2)_{2.43}(H)_{0.57}$ M. W. 271.4

Table 4 Ethyl Nitrate in Chloroform

Concentration: 1.043×10^{-5} mole/cc

Path Length Microns (1)		$\frac{I_o}{I}$	$A^{(2)}$	cm^{2a} $mole^{-1}$ (3)
b_I	b_t			
70	66.8	1.124	0.0508	7.29×10^5
100	96.5	1.178	0.0712	7.07×10^5
150	145.2	1.293	0.1116	7.37×10^5
200	195.5	1.410	0.1492	7.32×10^5
250	244.0	1.535	0.0861	7.31×10^5
300	293.8	1.663	0.2209	7.21×10^5
350	344.6	1.809	0.2574	7.16×10^5
400	394.1	1.965	0.2934	7.14×10^5
450	433.9	2.131	0.3286	7.10×10^5
500	492.9	2.344	0.3700	7.20×10^5
500	544.5	2.524	0.4021	7.08×10^5
600	594.5	2.750	0.4393	7.08×10^5
			Average	7.19×10^5

(1) b_I = Cell Micrometer Settings b_t = Measured Path Length

(2) A = Absorbance = $\log \left(\frac{I_o}{I} \right)$

(3) a = absorptivity = $\frac{A}{b_t \times c}$ c = mole/cc

Table 5 Ethyl Nitrate in Chloroform

Path Length (b_I): 70 microns

Concentration mole/cc	$\frac{I_o}{I}$	A	$cm^2 \cdot mole^{-1}$ a
1.27×10^{-5}	1.154	0.0622	7.34×10^5
2.20×10^{-5}	1.281	0.1076	7.32×10^5
4.31×10^{-5}	1.624	0.2106	7.32×10^5
6.60×10^{-5}	2.094	0.3210	7.28×10^5
8.08×10^{-5}	2.510	0.3997	7.41×10^5
10.96×10^{-5}	3.218	0.5076	6.93×10^5
		Average	7.27×10^5

Table 6 Amyl Nitrate in Chloroform

Concentration: 1.353×10^{-5} mole/cc

Path Length Microns b_I	b_t	$\frac{I_o}{I}$	A	a $cm^2 \cdot mole^{-1}$
70	66.8	1.1682	0.0674	7.46×10^5
100	96.5	1.2780	0.1065	7.85×10^5
150	145.2	1.4504	0.1614	8.21×10^5
200	195.5	1.6480	0.2170	8.20×10^5
250	244.1	1.8456	0.2662	8.06×10^5
300	293.8	2.0942	0.3210	8.08×10^5
350	344.6	2.3805	0.3768	8.08×10^5
400	394.1	2.6803	0.4281	8.03×10^5
450	443.9	2.9964	0.4765	7.93×10^5
500	492.9	3.3877	0.5299	7.94×10^5
550	544.5	3.8325	0.5833	7.92×10^5
600	594.5	4.3053	0.6340	7.88×10^5
			Average	7.97×10^5

Table 7 Amyl Nitrate in Chloroform

Path Length (b_I): 70 microns

Concentration Mole/cc	I_o	I	$\frac{I_o}{I}$	A	a $cm^2 \cdot mole^{-1}$
1.35×10^{-5}	10.3	77.3	1.1682	0.0674	7.47×10^5
3.62×10^{-5}	90.1	58.0	1.5534	0.1912	7.91×10^5
5.86×10^{-5}	98.8	44.2	2.0316	0.3079	7.87×10^5
7.43×10^{-5}	98.7	36.1	2.4848	0.3953	7.96×10^5
8.52×10^{-5}	89.2	32.0	2.7875	0.4453	7.82×10^5
1.01×10^{-4}	88.8	26.7	3.3258	0.5219	7.74×10^5
1.18×10^{-4}	88.7	21.8	4.0688	0.6100	7.74×10^5
1.38×10^{-4}	88.5	17.3	5.1156	0.7089	7.69×10^5
				Average	7.78×10^5

Table 8 Amyl Nitrate in Tetrahydrofuran

Path Length (b_I): 70 microns

Concentration mole/cc	$\frac{I_o}{I}$	A	a $cm^2 \cdot mole^{-1}$
2.51×10^{-5}	1.278	0.1066	6.36×10^5
4.56	1.905	0.2799	9.19×10^5
6.12	2.385	0.3775	9.23×10^5
7.81	3.003	0.4776	9.15×10^5
9.02	3.476	0.5411	8.98×10^5
10.74	4.335	0.6370	8.88×10^5
12.22	5.247	0.7199	8.82×10^5
			$\cancel{8.66 \times 10^5}$

Table 9   Ethylene Glycol Dinitrate in Chloroform

Concentration: 1.375×10^{-5} mole/cc

Path Length Microns		$\frac{I_o}{I}$	A	a $cm^2 \cdot mole^{-1}$
b_I	b_t			
100	96.5	1.5430	0.1884	14.20×10^5
200	195.5	2.3730	0.3753	13.96×10^5
300	293.8	3.6067	0.5571	13.79×10^5
400	394.1	5.3439	0.7278	13.43×10^5
500	492.9	7.9327	0.8994	13.27×10^5
550	544.5	9.8313	0.9926	13.26×10^5
			Average	13.65×10^5

Table 10 Ethylene Glycol Dinitrate in Chloroform
Path Length (b_I): 70 microns

Concentration mole/cc	$\frac{I_o}{I}$	A	$cm^2 \overset{a}{\cdot} mole^{-1}$
1.375×10^{-5}	1.3343	0.1253	13.64×10^5
3.908×10^{-5}	2.2897	0.3598	13.78×10^5
5.053×10^{-5}	2.8903	0.4610	13.66×10^5
6.560×10^{-5}	3.9427	0.5958	13.60×10^5
8.881×10^{-5}	6.0340	0.7784	13.12×10^5
10.184×10^{-5}	7.2789	0.8621	12.67×10^5
		Average	13.41×10^5

Table 11 Ethylene Glycol Dinitrate in Tetrahydroform

Concentration: 0.928×10^{-5} mole/cc

Path Length Microns b_I	b_t	$\frac{I_o}{I}$	A	$cm^2 \cdot mole^{-1}$
70	66.8	1.2436	0.0947	15.27×10^5
100	96.5	1.3825	0.1407	15.71×10^5
200	195.5	1.9168	0.2824	15.57×10^5
300	293.8	2.6380	0.4213	15.45×10^5
400	394.1	3.4901	0.5428	14.84×10^5
500	492.9	4.4925	0.6525	14.27×10^5
550	544.5	5.1404	0.7110	14.07×10^5
600	594.5	5.7702	0.7702	13.96×10^5
			Average	14.89×10^5

Table 12 **Ethylene Glycol Dinitrate in Tetrahydrofuran**

Path Length (b_I): 70 microns

Concentration mole/cc	$\frac{I_o}{I}$	A	$cm^2 \cdot mole^{-1}$
0.928×10^{-5}	1,2454	0.0952	15.36×10^5
2.296×10^{-5}	1.6757	0.2242	14.62×10^5
4.013×10^{-5}	2,4642	0.3917	14.61×10^5
6.382×10^{-5}	3.8080	0.5807	13.62×10^5
8.046×10^{-5}	5.5621	0.7452	13.86×10^5
10.526×10^{-5}	8.6122	0.9351	13.30×10^5
		Average	14.23×10^5

Table 13 Clycerol Trinitrate in Chloroform

Concentration: 0.452×10^{-5} mole/cc

Path Length Microns		$\frac{I_o}{I}$	A	$cm^2 \cdot mole^{-1}$
b_I	b_t			
100	96.5	1.2521	0.0976	22.08×10^5
200	195.5	1.5971	0.2033	22.70×10^5
300	293.8	2.0252	0.3465	25.75×10^5
400	394.1	2.5406	0.4049	22.43×10^5
500	492.9	3.2276	0.5089	22.54×10^5
550	544.5	4.0187	0.6041	24.23×10^5
			Average	23.29×10^5

Table 14 Glycerol Trinitrate in Chloroform

Path Length (b_I): 70 microns

Concentration mole/cc	$\frac{I_o}{I}$	A	cm^2 ‡ $mole^{-1}$
0.6 92 x 10^{-5}	1.2479	0.0962	20.82 x 10^5
1.612 x 10^{-5}	1.7148	0.2342	21.75 x 10^5
2.797 x 10^{-5}	2.5496	0.4064	21.75 x 10^5
3.489 x 10^{-5}	3.1767	0.5019	21.53 x 10^5
4.251 x 10^{-5}	4.0588	0.6085	21.43 x 10^5
5.026 x 10^{-5}	5.0452	0.6929	20.64 x 10^5
6.093 x 10^{-5}	6.7424	0.8288	20.36 x 10^5
		Average	21.18 x 10^5

Table 15 Glycerol Trinitrate in Tetrahydrofuran

Concentration: 0.956 x 10^{-5} mole/cc

Path Length Microns b_I	b_t	$\frac{I_0}{I}$	A	$cm^2 \cdot mole^{-1}$
70	66.8	1.3493	0.1301	20.38 x 10^5
100	96.5	1.5511	0.1793	19.44 x 10^5
200	195.5	2.4148	0.3829	20.50 x 10^5
300	293.8	3.6270	0.5596	19.93 x 10^5
400	394.1	5.2743	0.7222	19.17 x 10^5
500	492.9	7.2955	0.8631	18.33 x 10^5
600	594.5	10.1250	1.0054	17.69 x 10^5
			Average	19.35 x 10^5

Table 16 **Glycerol Trinitrate in Tetrahydrofuran**

Path Length (b_I): 70 microns

Concentration mole/cc	$\frac{I_o}{I}$	A	$cm^2 \overset{a}{\cdot} mole^{-1}$
0.956×10^{-5}	1.3493	0.1301	20.37×10^5
1.388×10^{-5}	1.5344	0.1859	20.05×10^5
2.229×10^{-5}	1.9954	0.3000	20.15×10^5
3.647×10^{-5}	2.9655	0.4721	19.38×10^5
4.352×10^{-5}	3.6810	0.5660	19.47×10^5
5.943×10^{-5}	5.4839	0.7391	18.62×10^5
7.256×10^{-5}	7.5525	0.8787	18.13×10^5
		Average	19.45×10^5

Table 17. Cellulose Nitrate (12.53% N) in Tetrahydrofuran

Concentration: 1.226×10^{-5} mole/cc

Path Length Microns b_I	b_t	$\frac{I_o}{I}$	A	$a_2(NO_2)$ $cm^2 \cdot mole^{-1}$
70	66.8	1.0927	0.0285	4.70×10^5
100	96.5	1.1363	0.0555	4.69×10^5
200	195.5	1.2868	0.1095	4.57×10^5
300	293.8	1.4721	0.1679	4.66×10^5
400	394.1	1.6685	0.2225	4.53×10^5
500	492.9	1.8780	0.2737	4.53×10^5
600	594.5	2.1268	0.3278	4.50×10^5
			Average	4.60×10^5

Table 18 Cellulose Nitrate (12.53%N) in Tetrahydrofuran

Concentration: 2.380×10^{-5} mole NO_2/cc

Path Length		$\frac{I_o}{I}$	A	ε (NO_2) $cm^2 \cdot mole^{-1}$
b_I	b_t			
70	66.8	1.1957	0.0873	4.93×10^5
100	96.5	1.2935	0.1119	4.87×10^5
200	195.5	1.6395	0.2148	4.62×10^5
300	293.8	2.1043	0.3231	4.62×10^5
400	394.1	2.6327	0.4205	4.48×10^5
500	492.9	3.3369	0.5234	4.46×10^5
600	594.5	4.240	0.6274	4.43×10^5
			Average	4.63×10^5

Table 19 Cellulose Nitrate (12.53% N) in Tetrahydrofuran

Concentration: 3.624×10^{-5} mole (NO_2)/cc

Path Length Microns b_I	b_t	$\frac{I_o}{I}$	A	$a_2(NO_2)$ $cm^2 \cdot mole^{-1}$
70	66.8	1.2999	0.1139	4.71×10^5
100	96.5	1.4721	0.1676	4.79×10^5
200	195.5	2.1278	0.3280	4.63×10^5
300	293.8	3.0144	0.4791	4.50×10^5
400	394.1	4.3315	0.6367	4.46×10^5
500	492.9	5.833	0.7659	4.29×10^5
600	594.5	7.7961	0.8918	4.14×10^5
			Average	4.50×10^5

Table 20 Cellulose Nitrate (12.53% N) in Tetrahydrofuran

Concentration: 6.827×10^{-5} mole (NO_2)/cc

Path Length Microns b_I	b_t	$\frac{I_o}{I}$	A	$a_2(NO_2)$ $cm^2 \cdot mole^{-1}$
70	66.8	1.6245	0.2109	4.63×10^5
100	96.5	2.0145	0.3043	4.62×10^5
200	195.5	3.8727	0.5881	4.41×10^5
300	293.8	7.0416	0.8477	4.23×10^5
400	394.1	11.9166	1.0763	4.00×10^5
500	492.9	1[illegible].1923	1.2093	3.59×10^5
600	594.5	21.4054	1.3306	3.28×10^5
			Average	4.11×10^5

Table 21 Cellulose Nitrate (12.53% N) in Tetrahydrofuran

Concentration: 10.549×10^{-5} mole NO_2/cc

Path Length Microns b_I	b_t	$\frac{I_o}{I}$	A	a (NO_2) cm^2 $mole^{-1}$
70	66.8	2.1618	0.3349	4.75×10^5
100	96.5	3.1126	0.4932	4.84×10^5
200	195.5	9.4086	0.9735	4.72×10^5
300	293.8	34.0370	1.5320	4.94×10^5
400	394.1	—	—	—
500	492.9	—	—	—
600	594.5	—	—	—
			Average	4.81×10^5

Table 22 Cellulose Nitrate (12.53% N) in Tetrahydrofuran

Path Length (b_I): 100 microns

Concentration Mole NO_2/cc	$\frac{I_o}{I}$	A	$a_2(NO_2)$ $cm^2 \cdot mole^{-1}$
1.226×10^{-5}	1.1363	0.0555	4.69×10^5
2.380×10^{-5}	1.2935	0.1119	4.87×10^5
3.624×10^{-5}	1.4721	0.1676	4.79×10^5
6.827×10^{-5}	2.0145	0.3043	4.62×10^5
10.549×10^{-5}	3.1126	0.4932	4.84×10^5
		Average	4.76×10^5

Table 23 Cellulose Nitrate (12.53% N) in Tetrahydrofuran

Path Length (b_I): 200 microns

Concentration mole NO_2/cc	$\frac{I_o}{I}$	A	$a_2(NO_2)$ $cm^2 \cdot mole^{-1}$
1.226×10^{-5}	1.2868	0.1095	4.57×10^5
2.380×10^{-5}	1.6395	0.2148	4.62×10^5
3.624×10^{-5}	2.1278	0.3280	4.63×10^5
6.827×10^{-5}	3.872	0.5881	4.41×10^5
10.549×10^{-5}	9.4086	0.9735	4.72×10^5
		Average	4.59×10^5

Table 24 Cellulose Nitrate (12.53% N) in Tetrahydrofuran

Path Length (b_I): 300 microns

Concentration mole NO_2/cc	$\frac{I_o}{I}$	A	a (NO_2) $cm^2 \cdot mole^{-1}$
1.226×10^{-5}	1.4721	0.1679	4.66×10^5
2.380×10^{-5}	2.1043	0.3231	4.62×10^5
3.624×10^{-5}	3.0144	0.4791	4.50×10^5
6.827×10^{-5}	7.0416	0.8477	4.23×10^5
10.549×10^{-5}	3.4037	1.5320	4.94×10^5
		Average	4.59×10^5

Table 25 Cellulose Nitrate (12.53% N) in Tetrahydrofuran

Path Length (b_I): 400 microns

Concentration mole NO_2/cc	$\frac{I_o}{I}$	A	a (NO_2) $cm^2 \cdot mole^{-1}$
1.226×10^{-5}	1.6685	0.2225	4.66×10^5
2.380×10^{-5}	2.6327	0.4205	4.48×10^5
3.624×10^{-5}	4.3315	0.6367	4.46×10^5
6.827×10^{-5}	11.9166	1.0763	4.00×10^5
10.549×10^{-5}	—	—	—
		Average	4.40×10^5

Table 26 Cellulose Nitrate (12.53% N) in Tetrahydrofuran

Path Length (b_I): 500 microns

Concentration mole NO_2/cc	$\frac{I_o}{I}$	A	ϵ (NO_2) $cm^2 \cdot mole^{-1}$
1.226×10^{-5}	1.8780	0.2737	4.53×10^5
2.380×10^{-5}	3.3369	0.5234	4.46×10^5
3.624×10^{-5}	5.8333	0.7659	4.29×10^5
6.827×10^{-5}	16.1923	1.2093	3.59×10^5
10.549×10^{-5}	—	—	—
		Average	4.22×10^5

Table 27 Cellulose Nitrate (12.53% N) in Tetrahydrofuran

Path Length (b_I): 600 microns

Concentration mole NO_2/cc	$\frac{I_o}{I}$	A	a (NO_2) $cm^2 \cdot mole^{-1}$
1.226×10^{-5}	2.1268	0.3278	4.50×10^5
2.380×10^{-5}	4.240	0.6274	4.43×10^5
3.624×10^{-5}	7.7961	0.8918	4.14×10^5
6.827×10^{-5}	21.4054	1.3306	3.28×10^5
10.549×10^{-5}	——	——	——
		Average	4.09×10^5

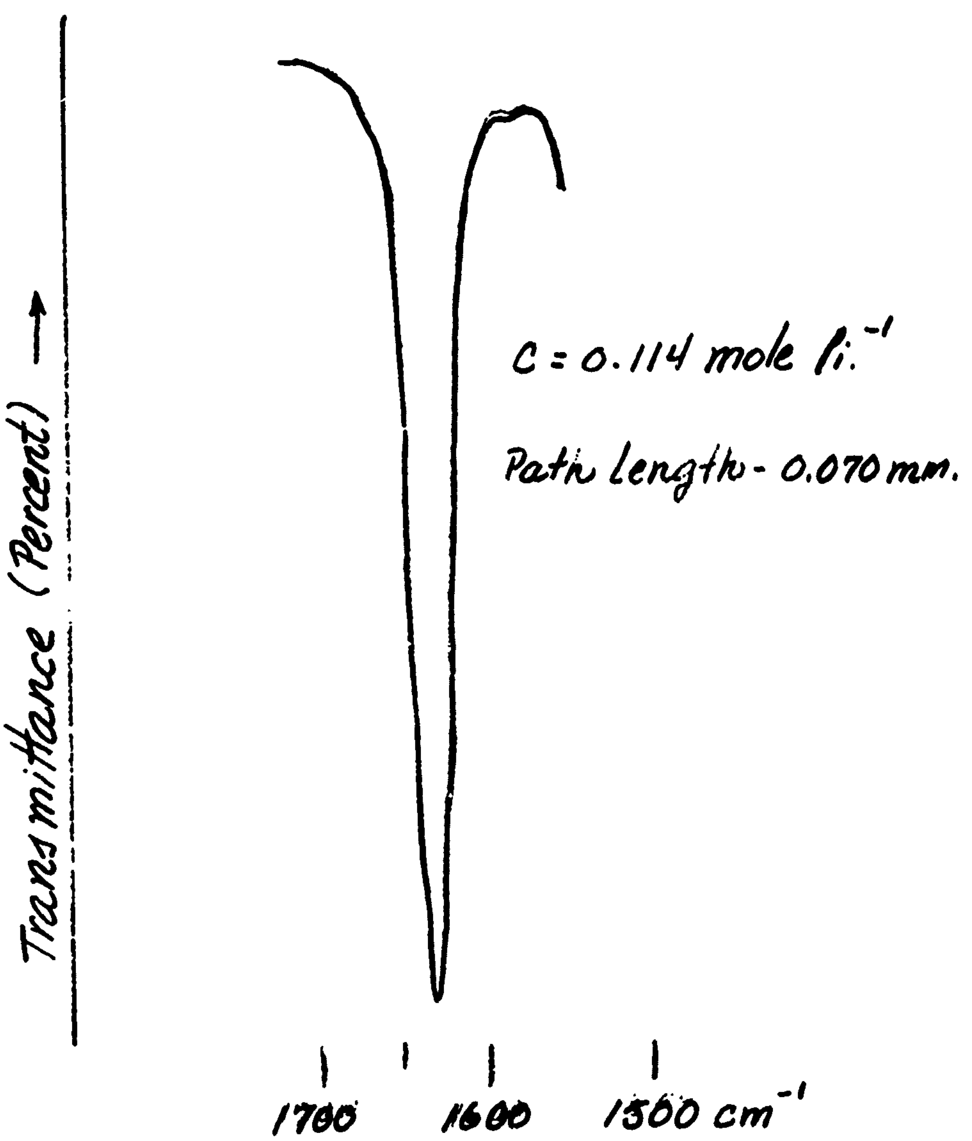

Fig. 1 Asymmetric N=O Stretch of Ethyl Nitrate in Chloroform.

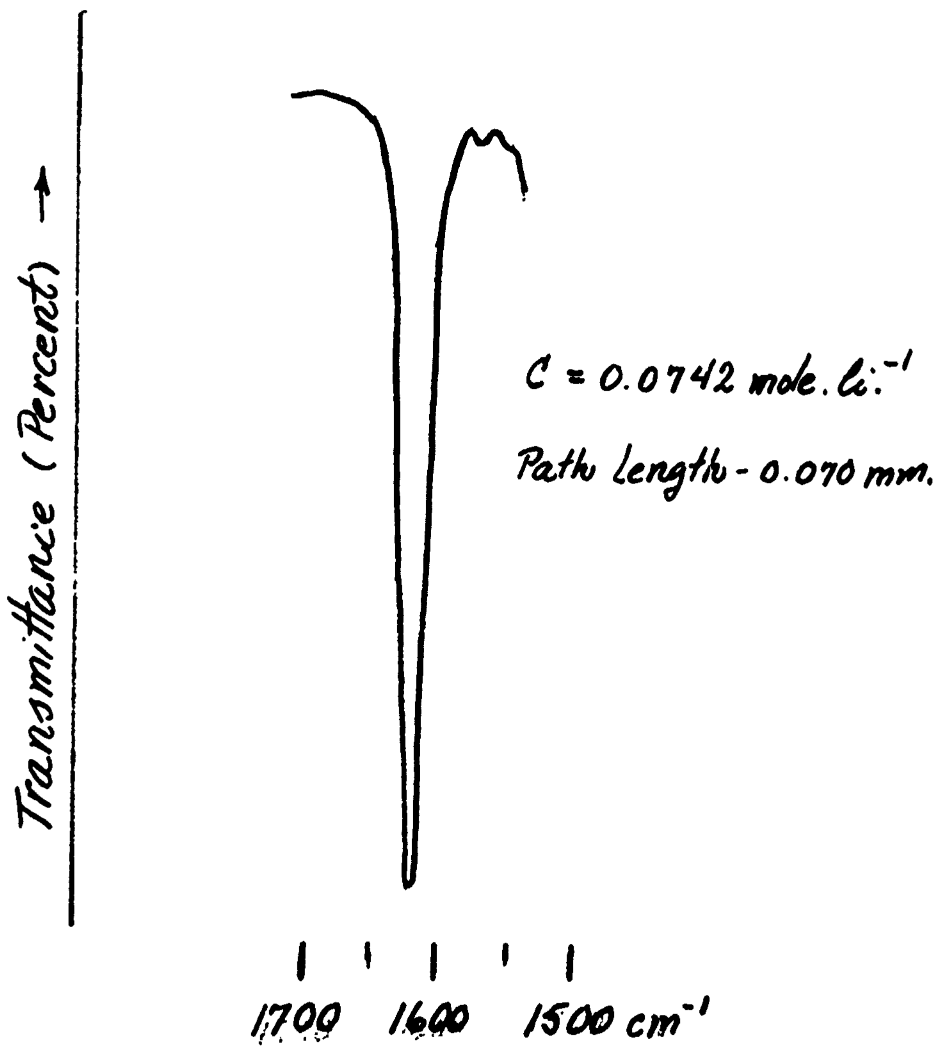

Fig. 2 Asymmetric N=O Stretch of Amyl Nitrate in Chloroform.

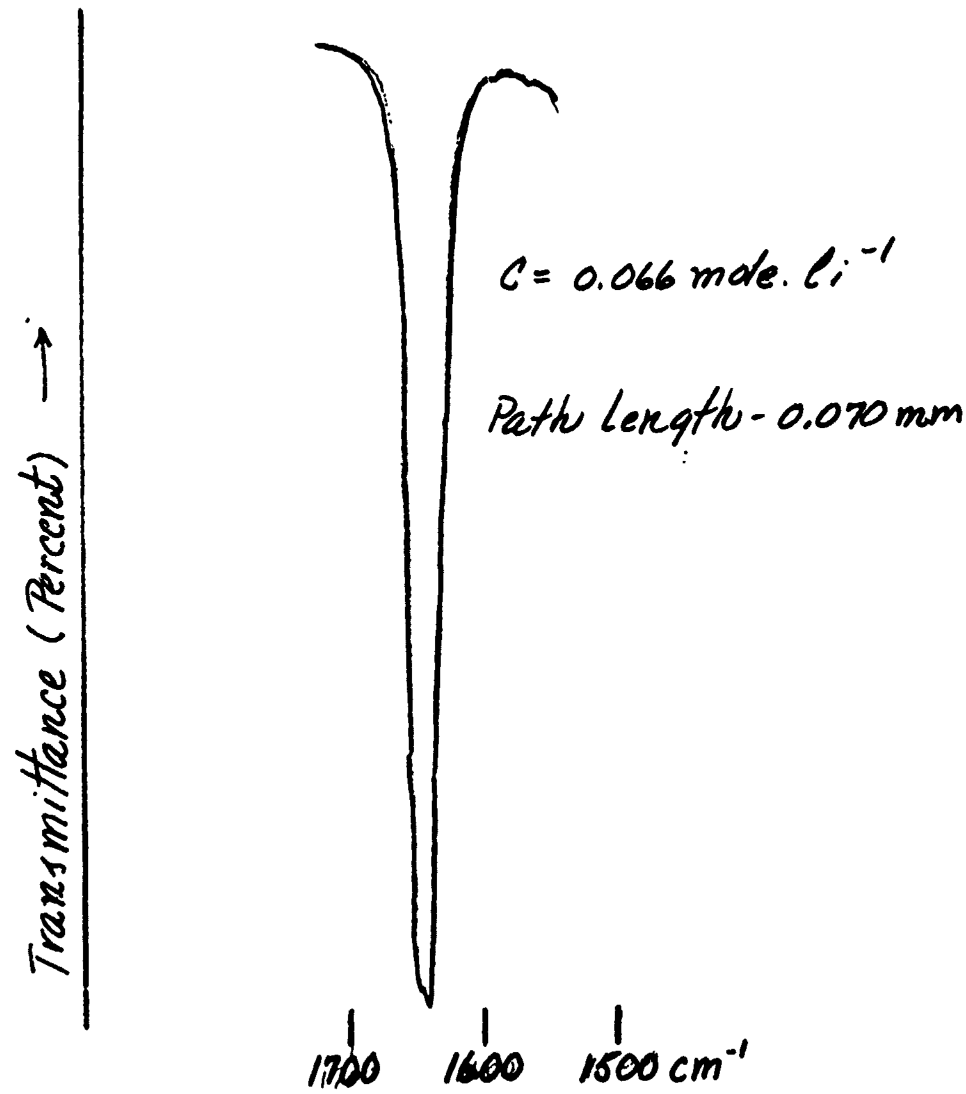

Fig. 3 Asymmetric N=O Stretch of Ethylene Glycol Dinitrate in Chloroform.

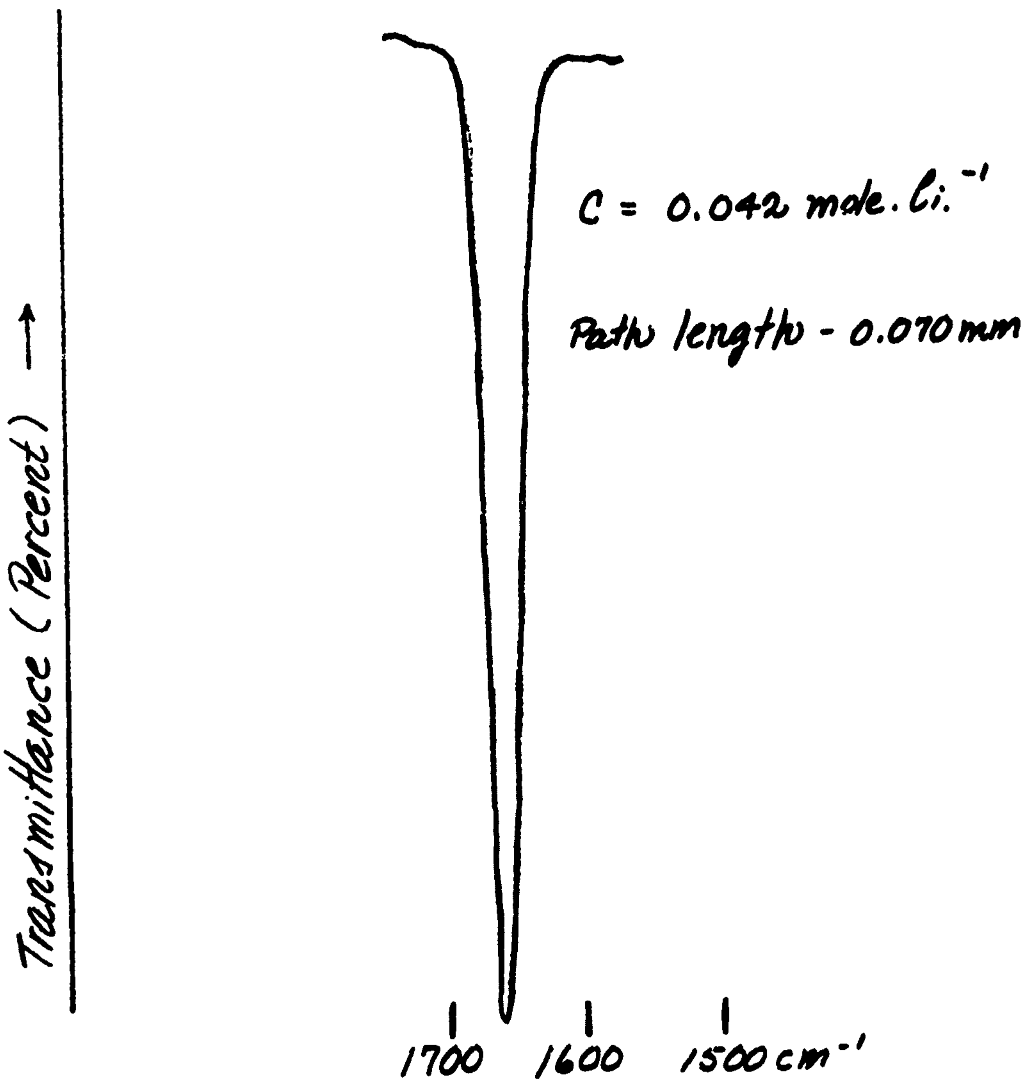

Fig. 4 Asymmetric N=O stretch for Glycerol Trinitrate in Chloroform.

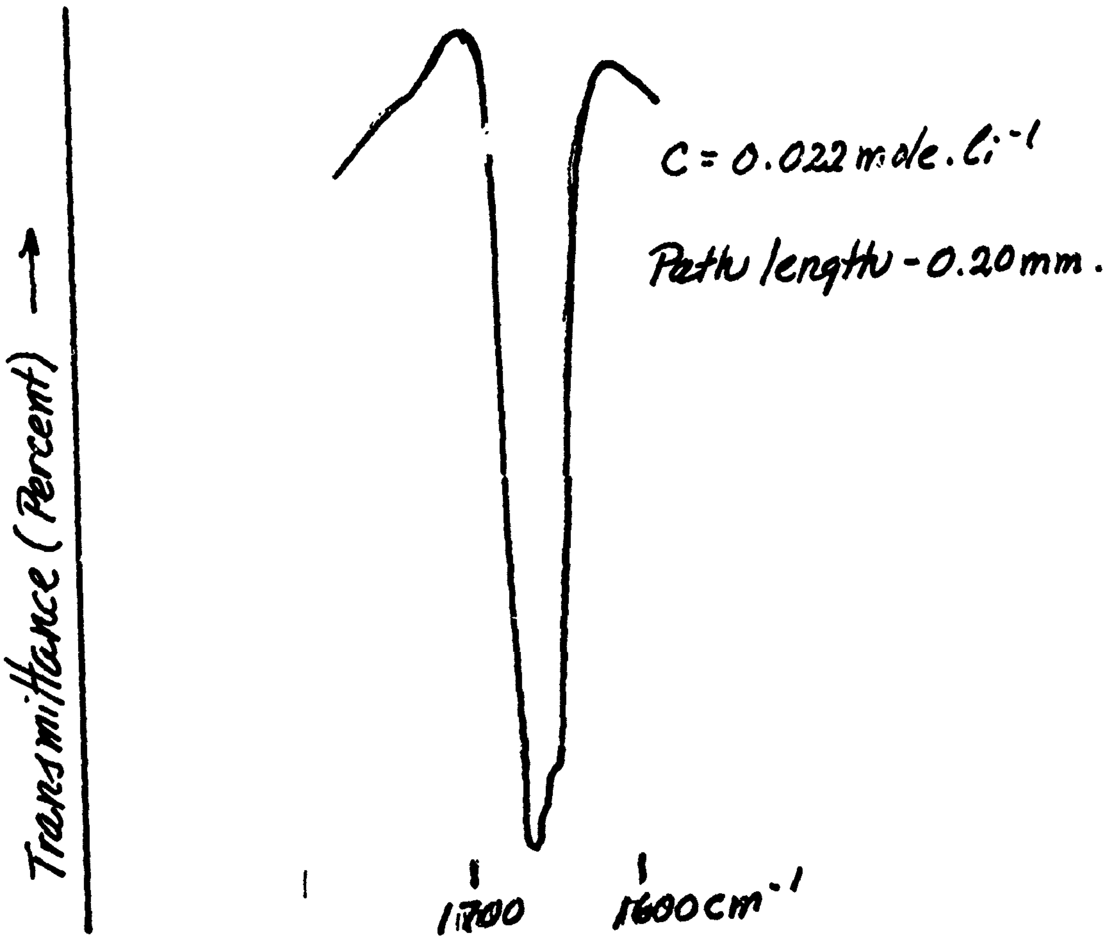

Fig. 5 Asymmetric N=O stretch of Cellulose Nitrate (12.53%N) in Tetrahydrofuran.

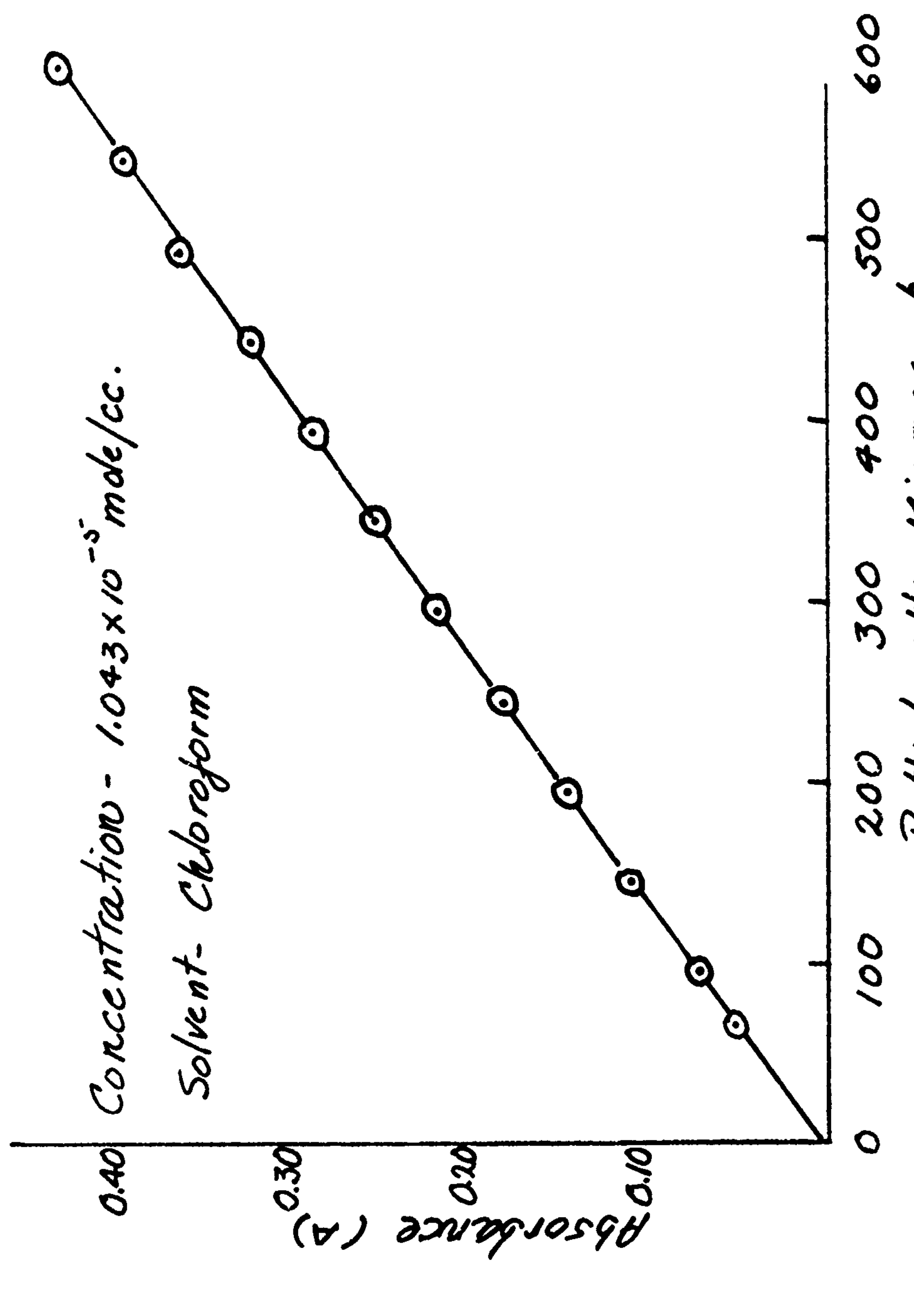

Fig. 6 Ethyl Nitrate - A vs b_t

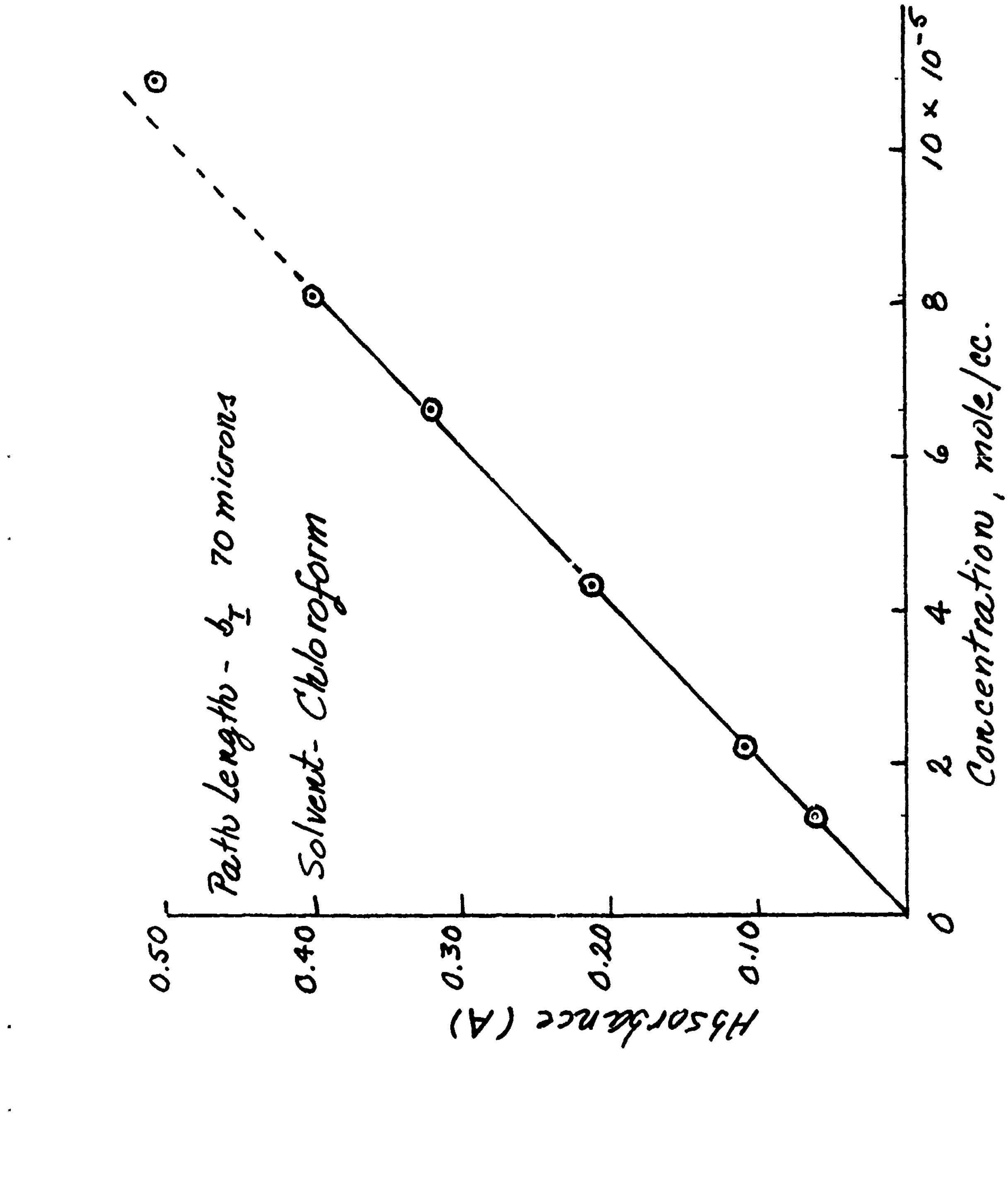

FIG. 7 Ethyl Nitrate - A vs Concentration.

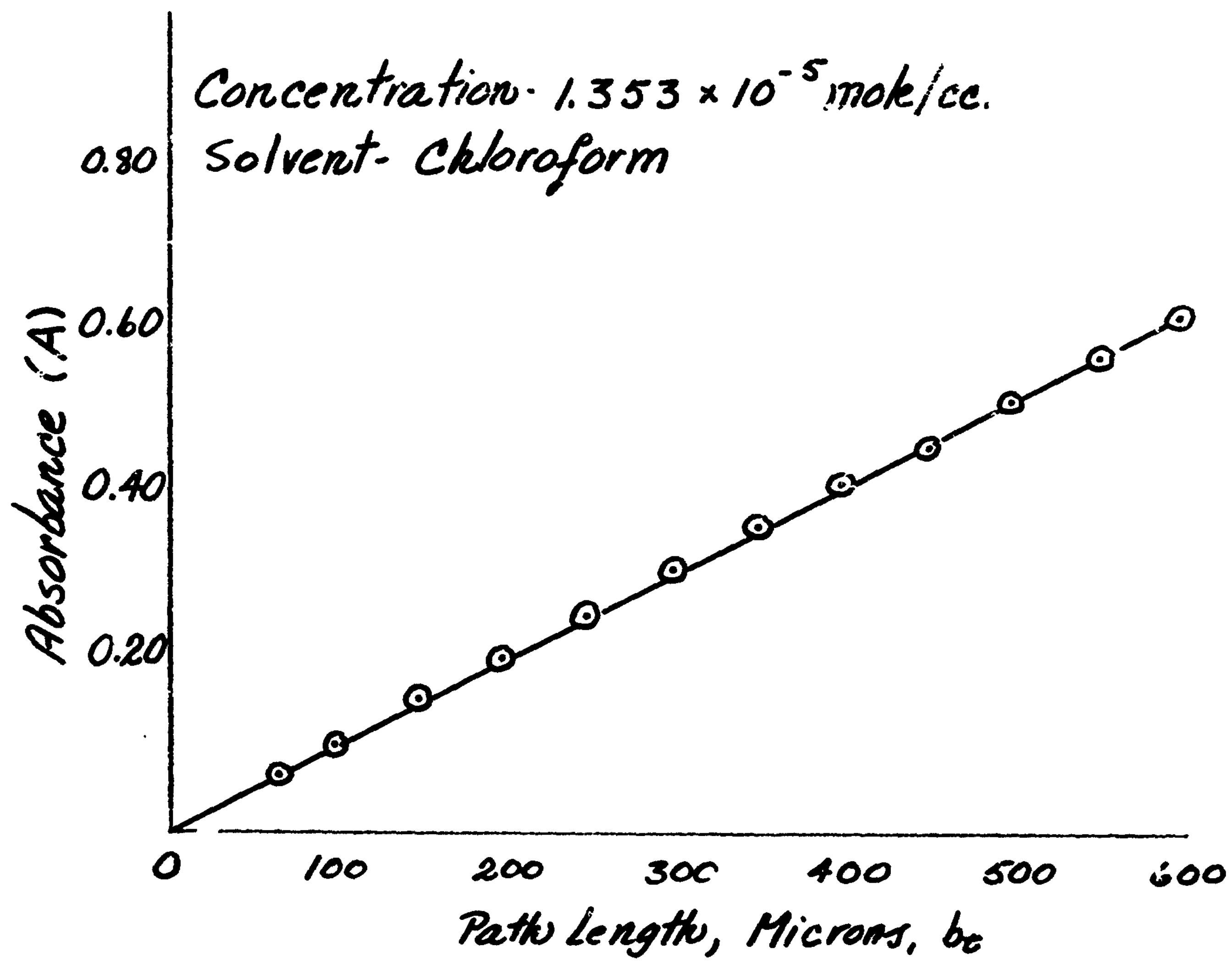

Fig. 8 Amyl Nitrate - A vs b_c

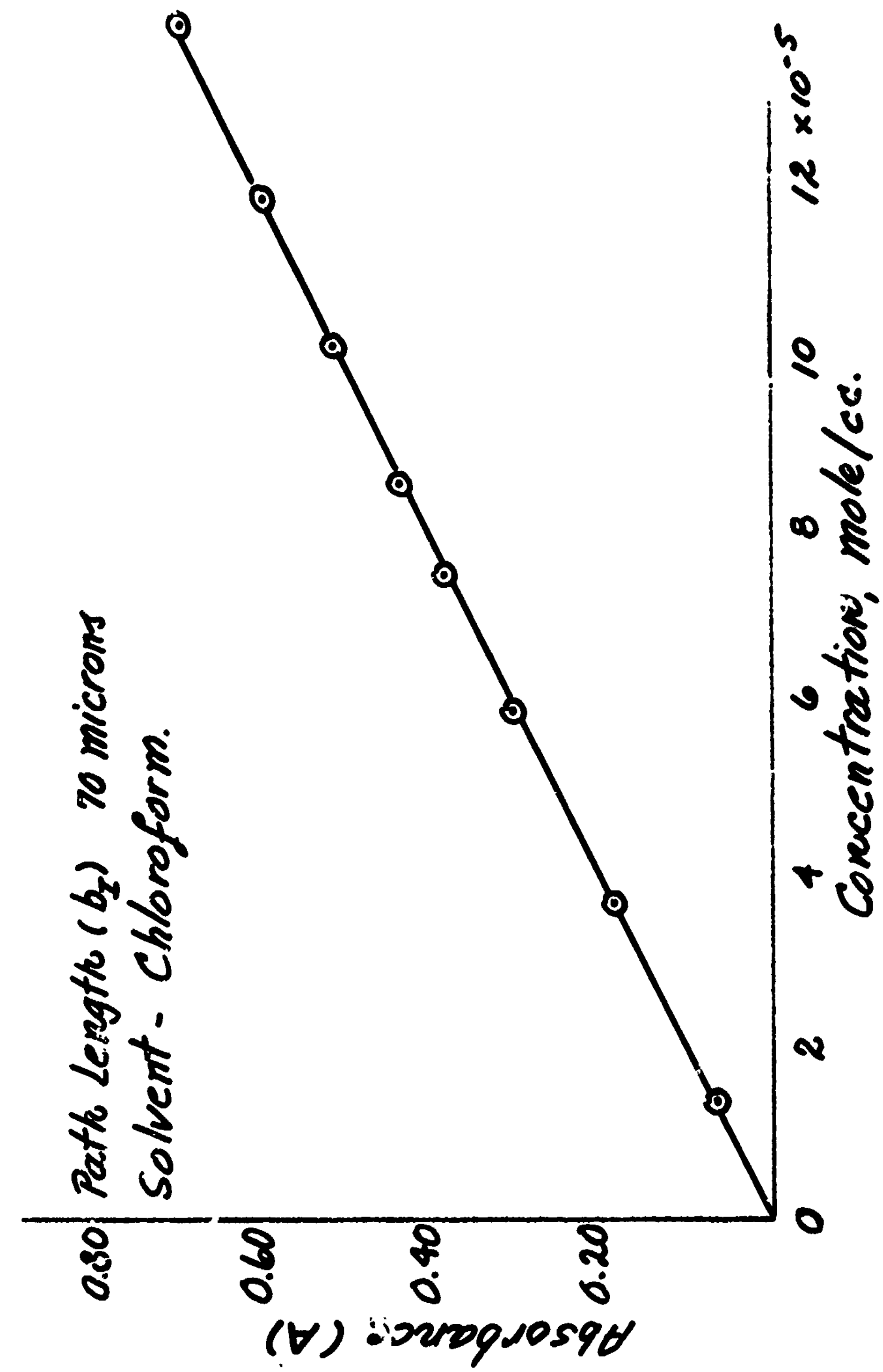

Fig. 9 Amyl Nitrate - A vs Concentration.

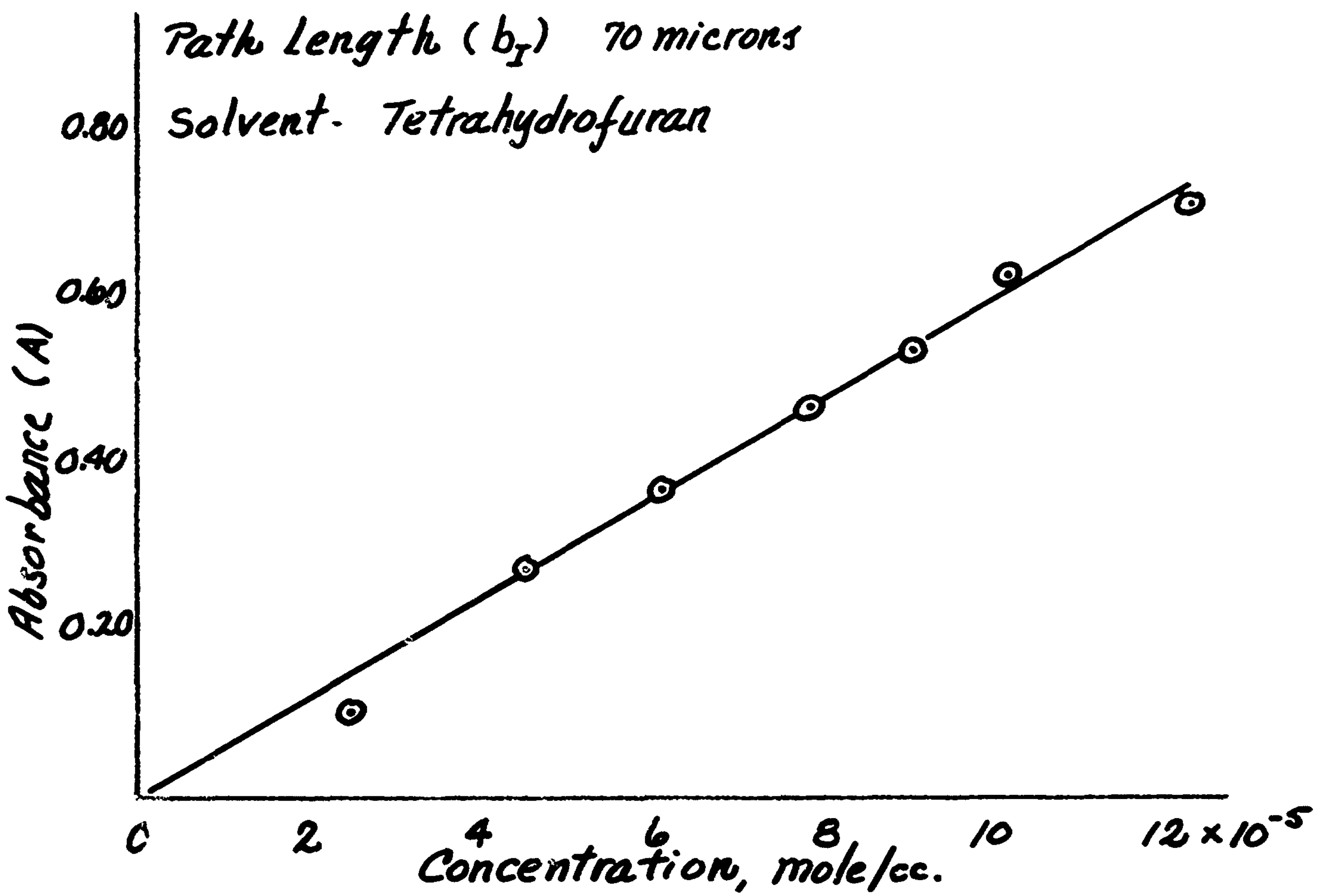

Fig. 10 Amyl Nitrate - A vs Concentration.

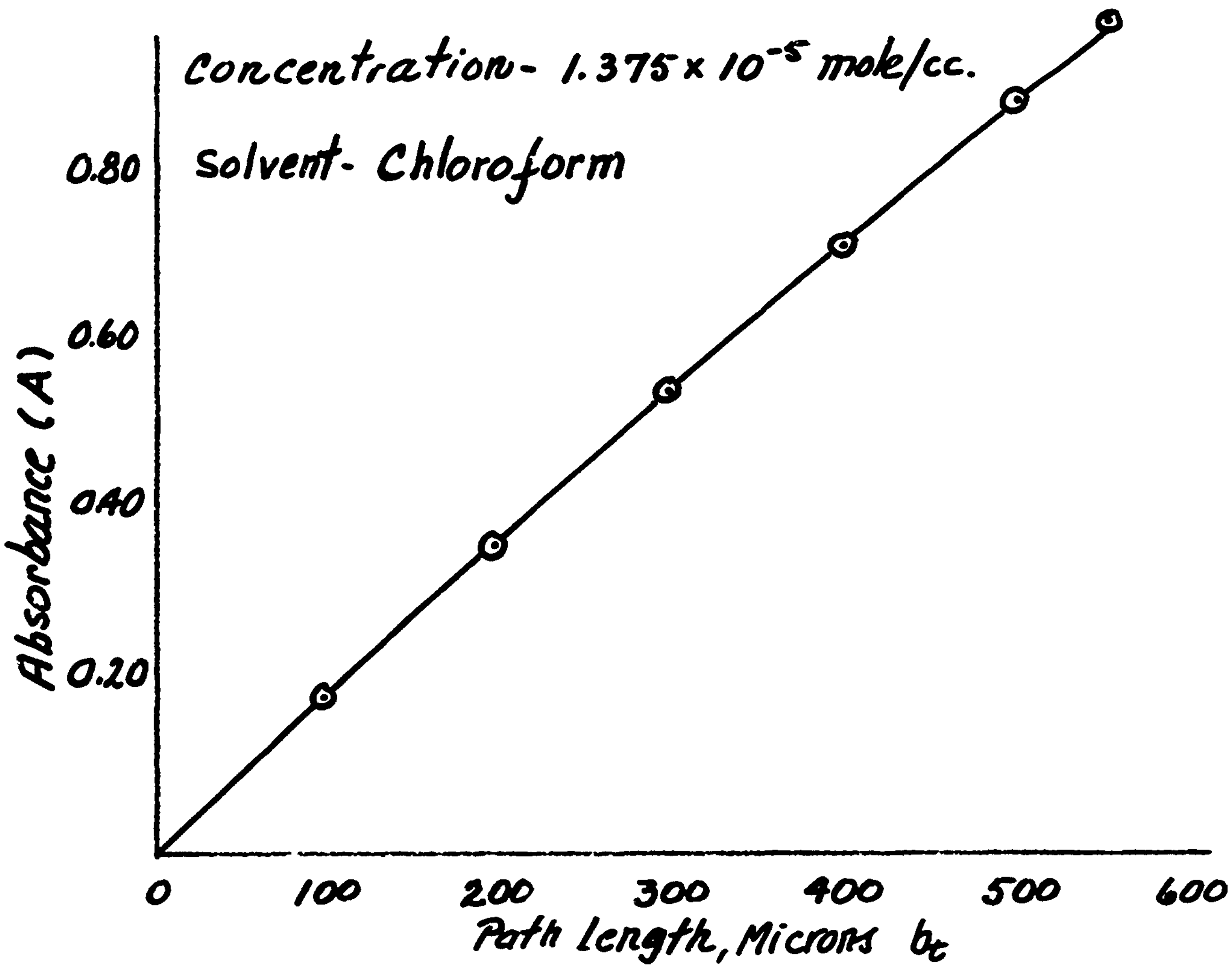

Fig. 11 Ethylene Glycol Dinitrate- A vs b_c

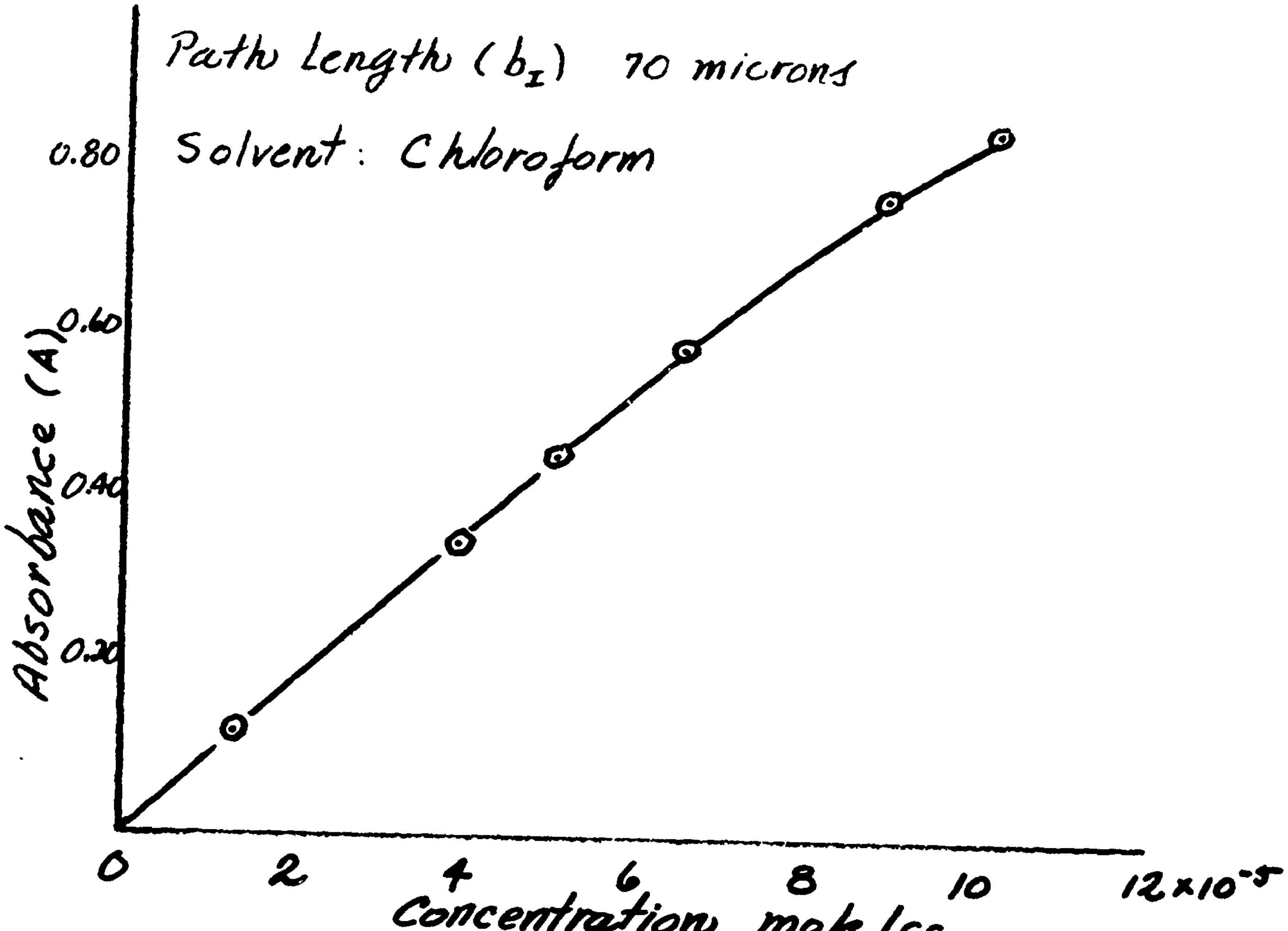

FIG. 12 Ethylene Glycol Dinitrate - A vs Concentration

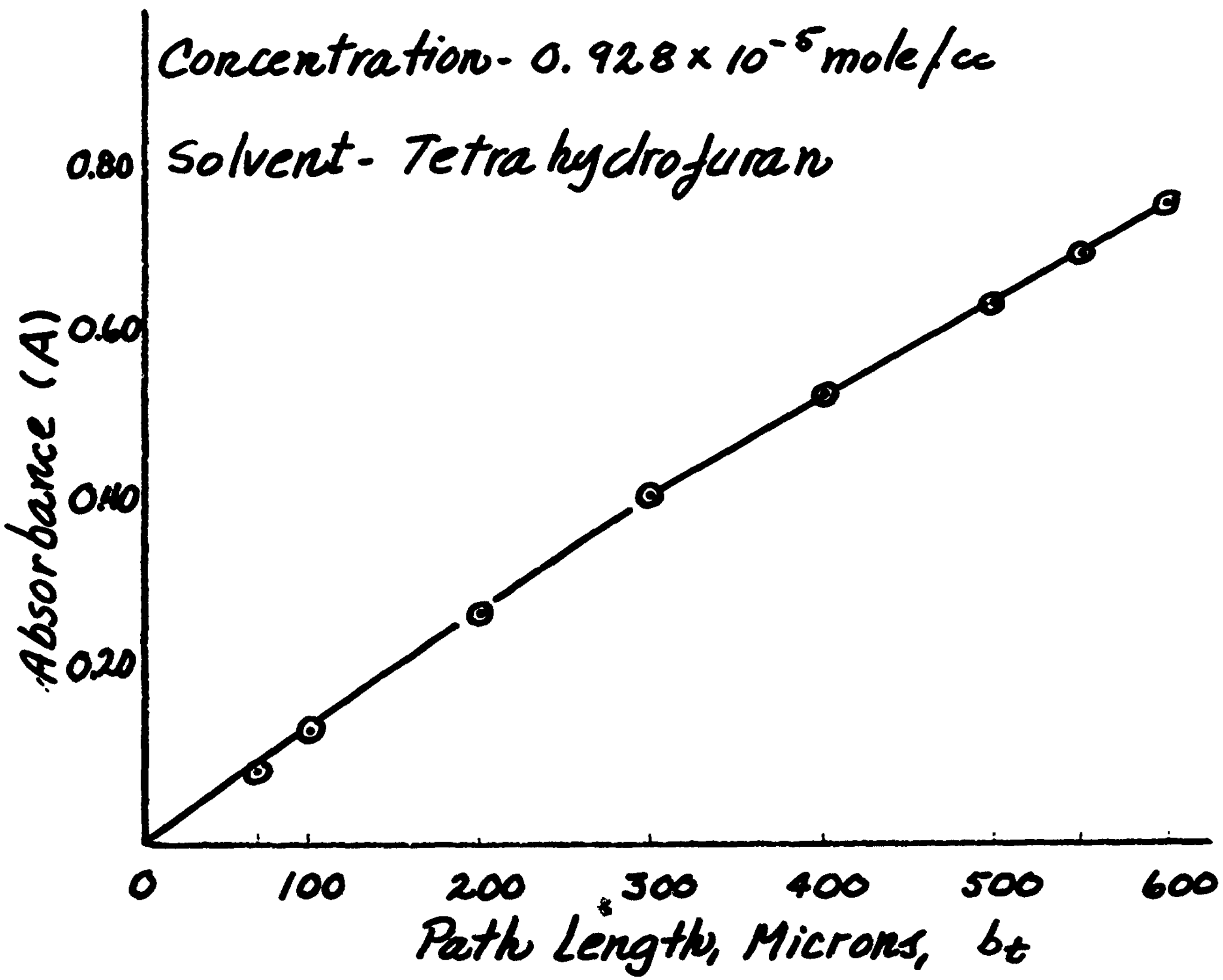

Fig. 13 Ethylene Glycol Dinitrate - A vs b_t

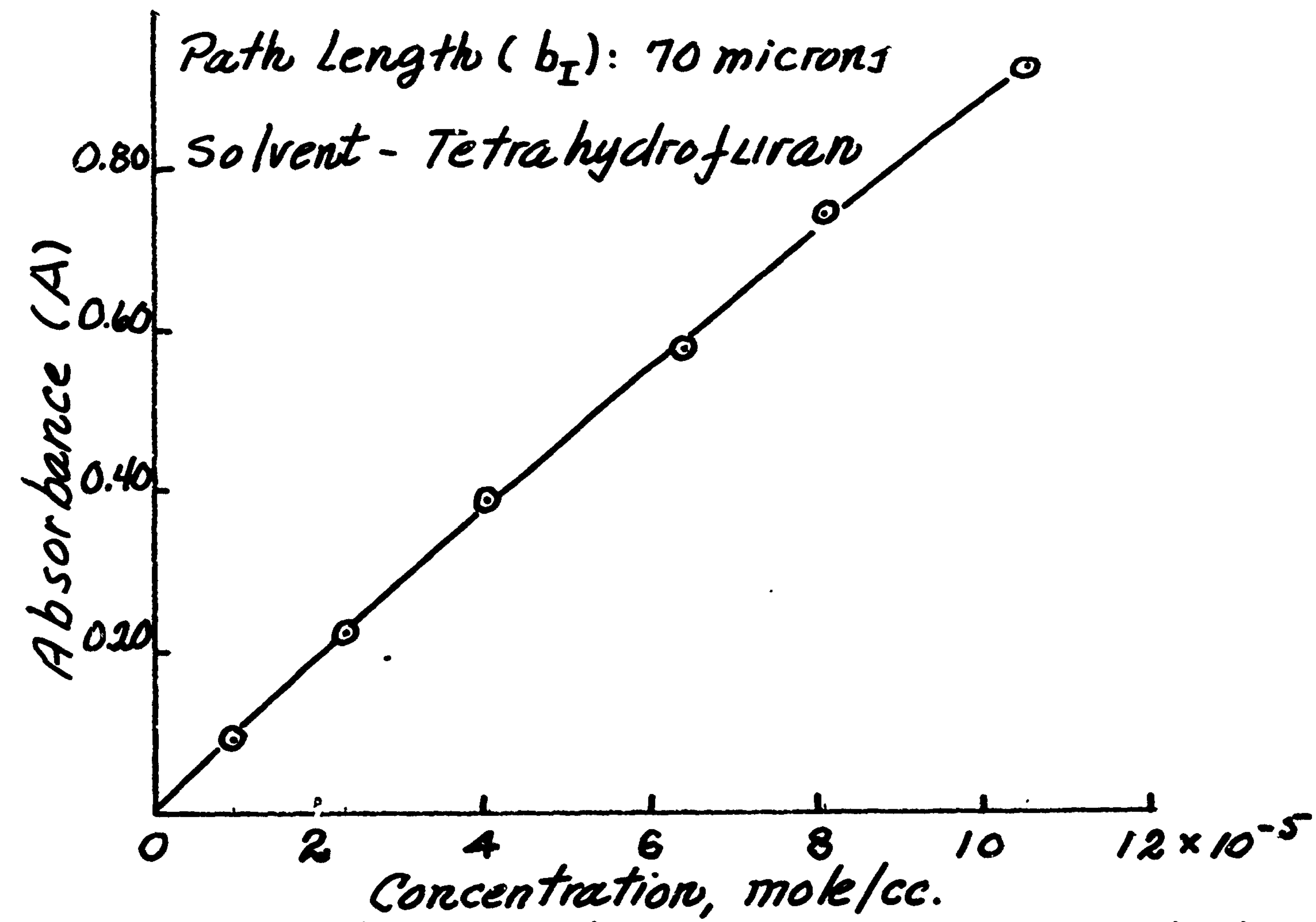

FIG. 14 Ethylene Glycol Dinitrate- A vs Concentration

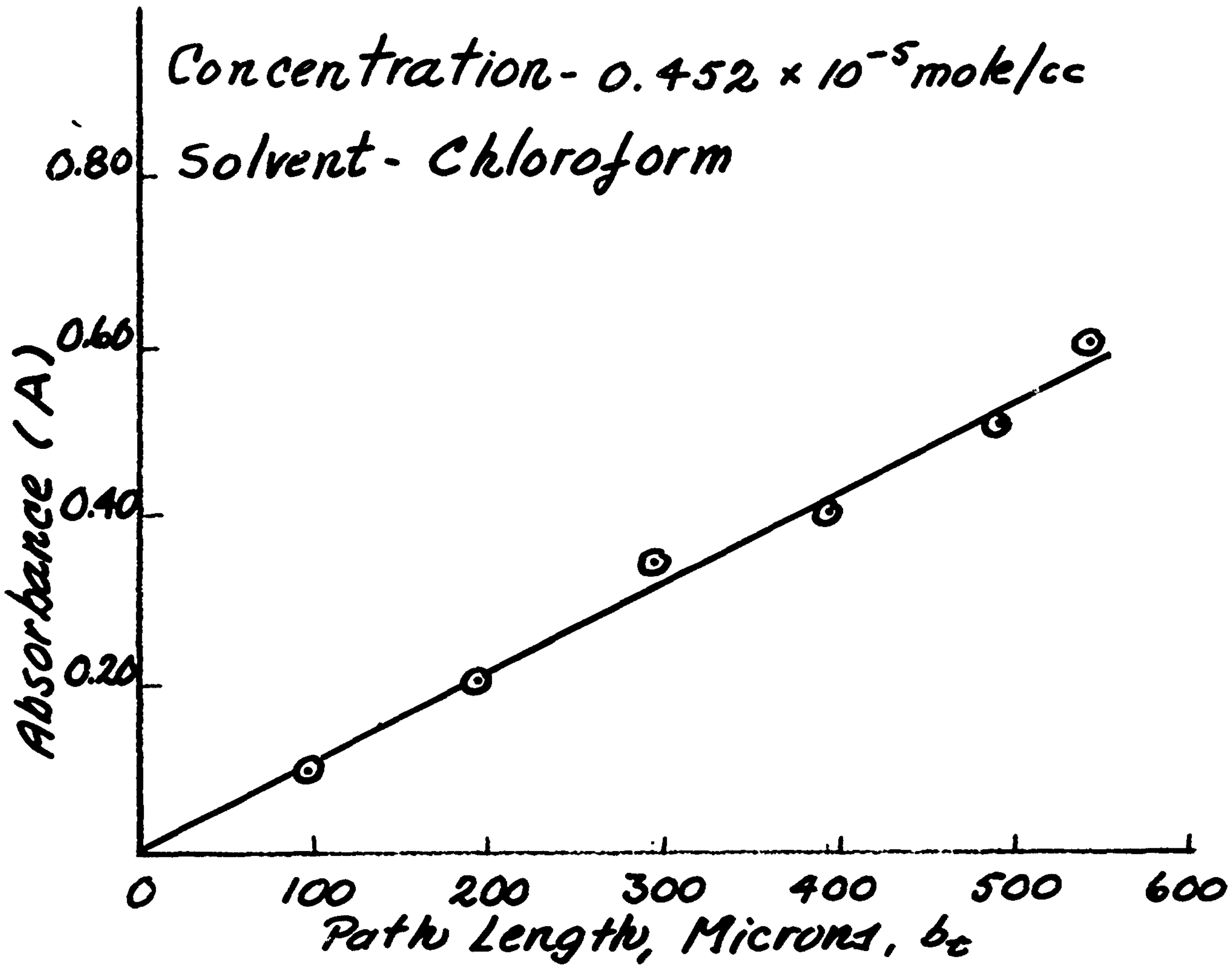

Fig. 15 Glycerol Trinitrate - A vs b_t

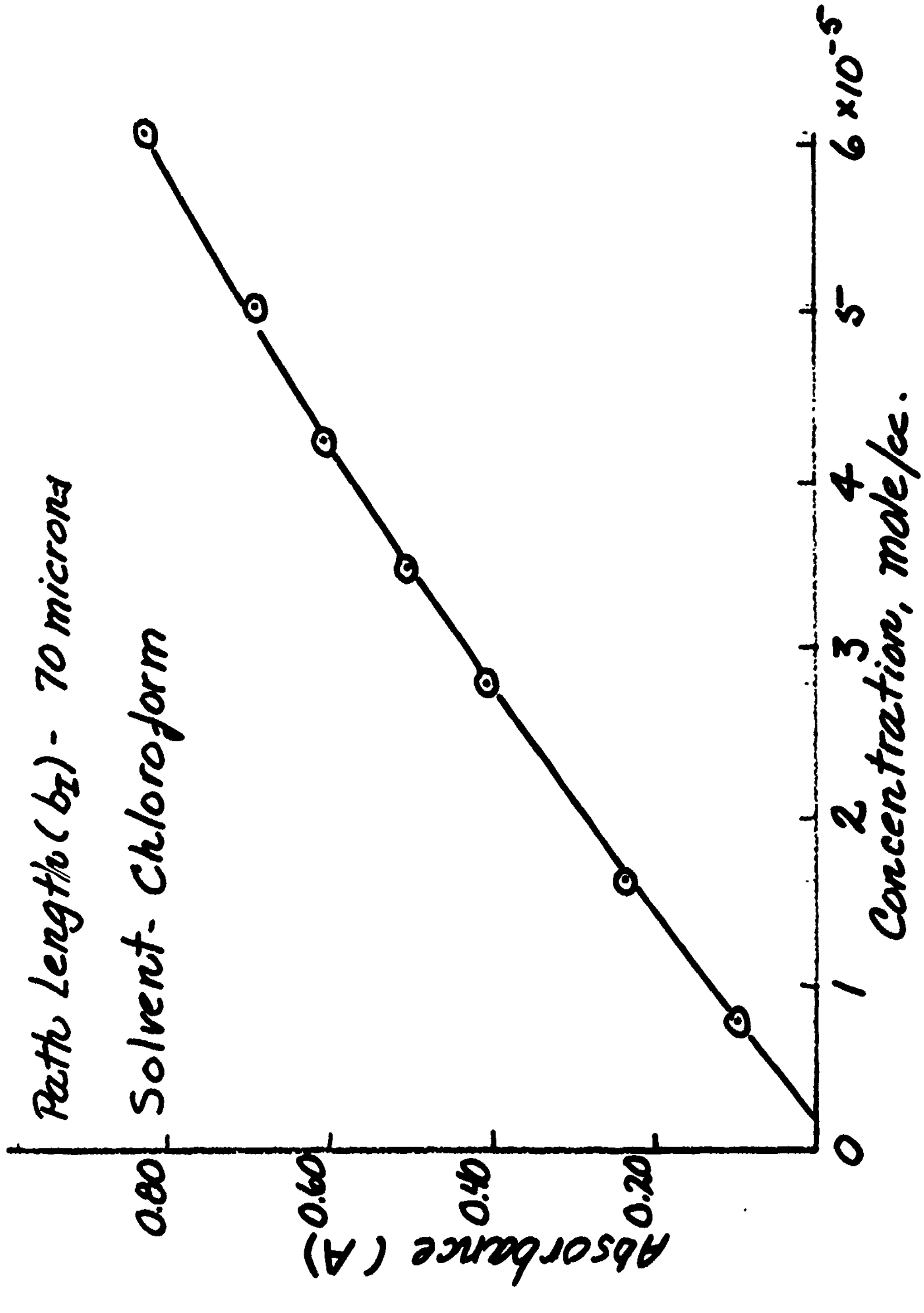

FIG. 16 Glycerol Trinitrate - A vs Concentration

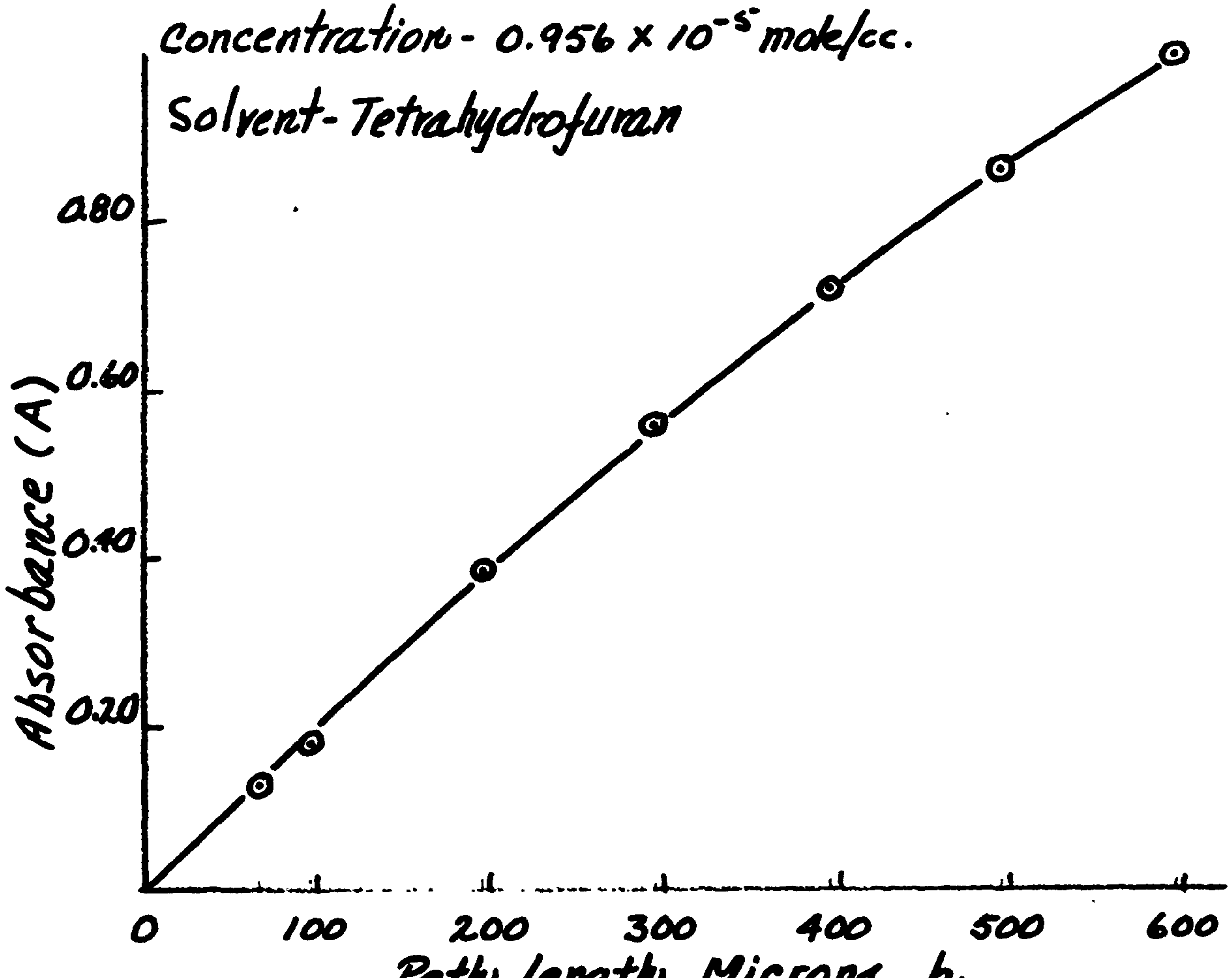

Fig. 17 Glycerol Trinitrate - A vs b_t

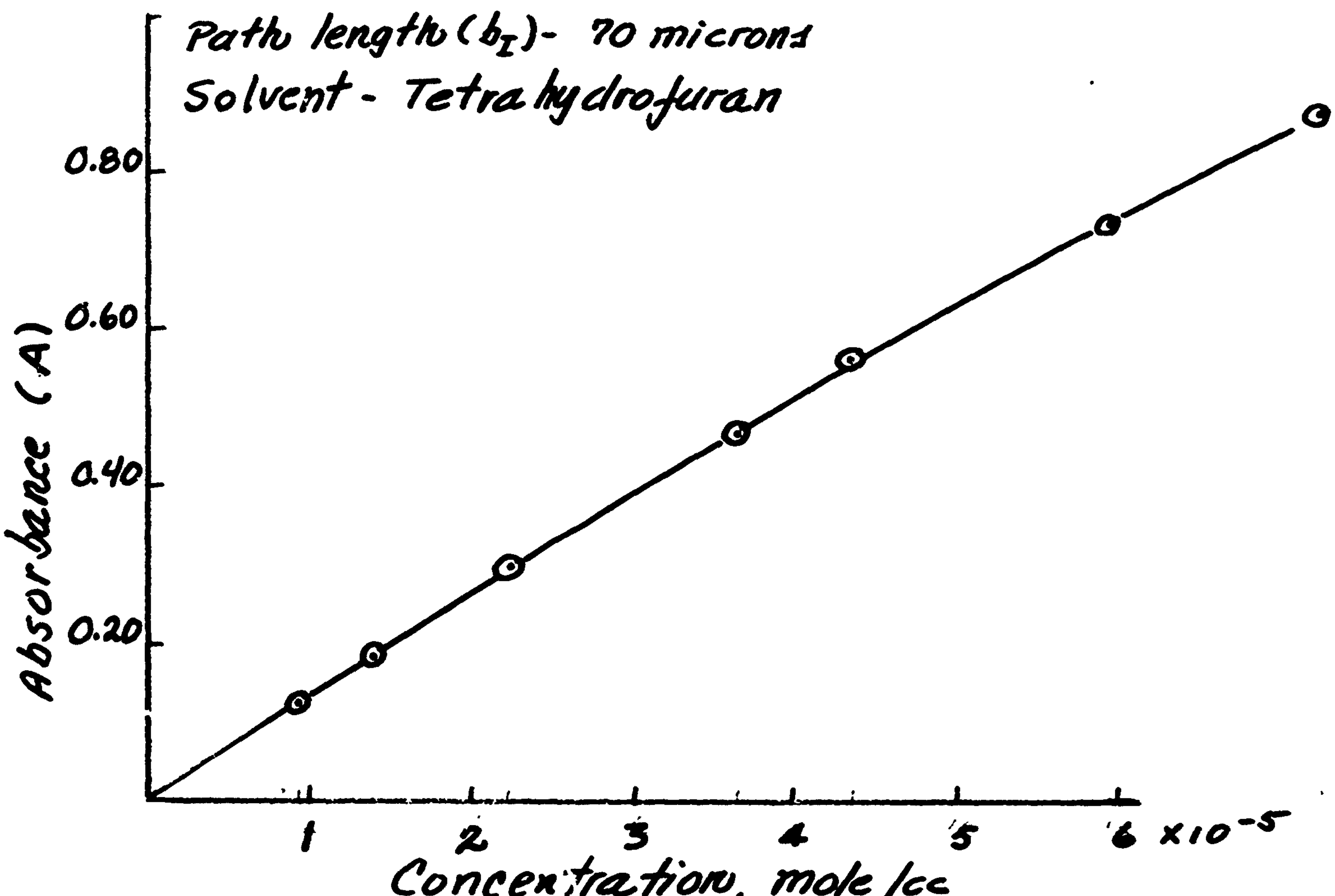

FIG. 18 Glycerol Trinitrate - A vs Concentration.

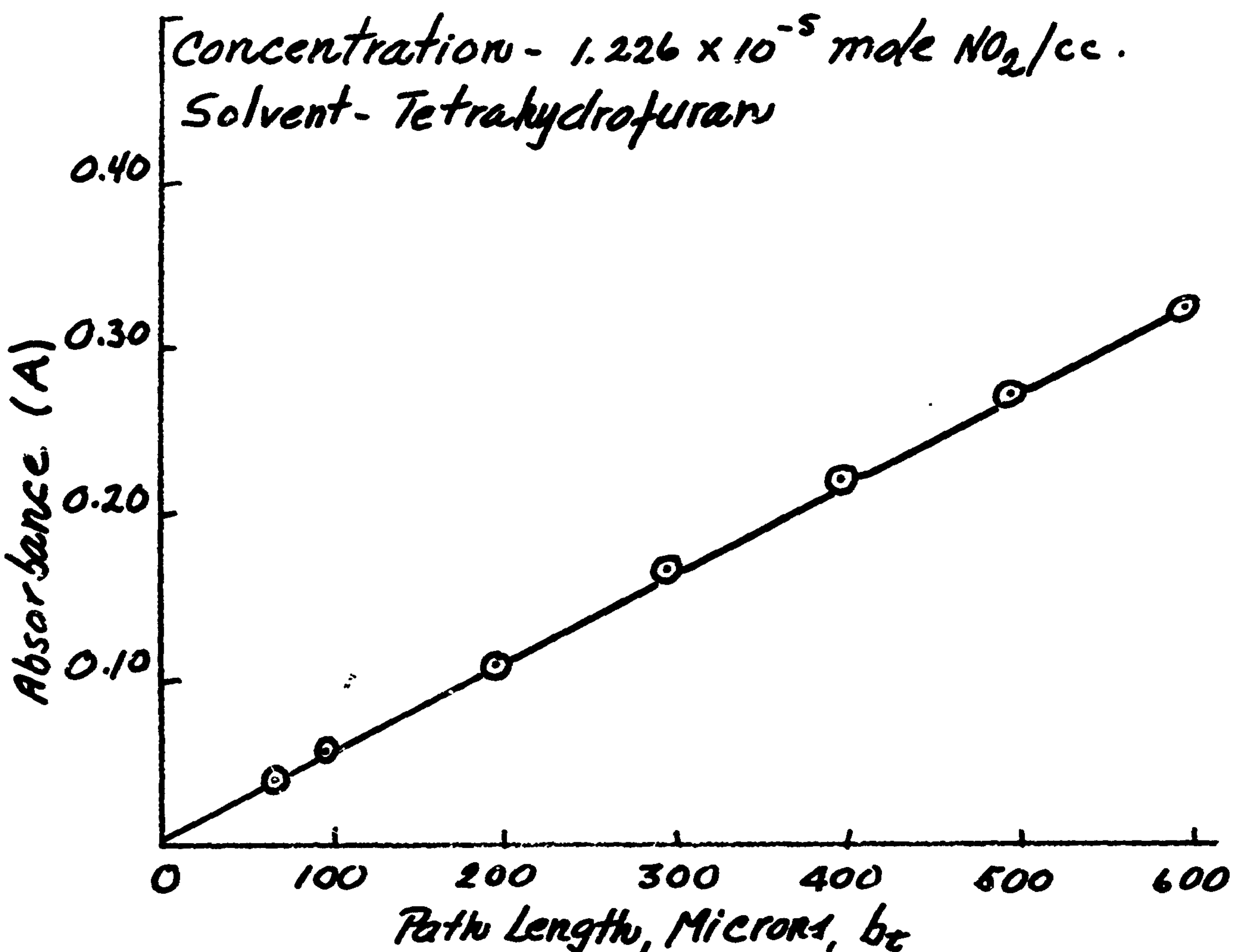

Fig. 19 Cellulose Nitrate (12.53% N) A vs b_t

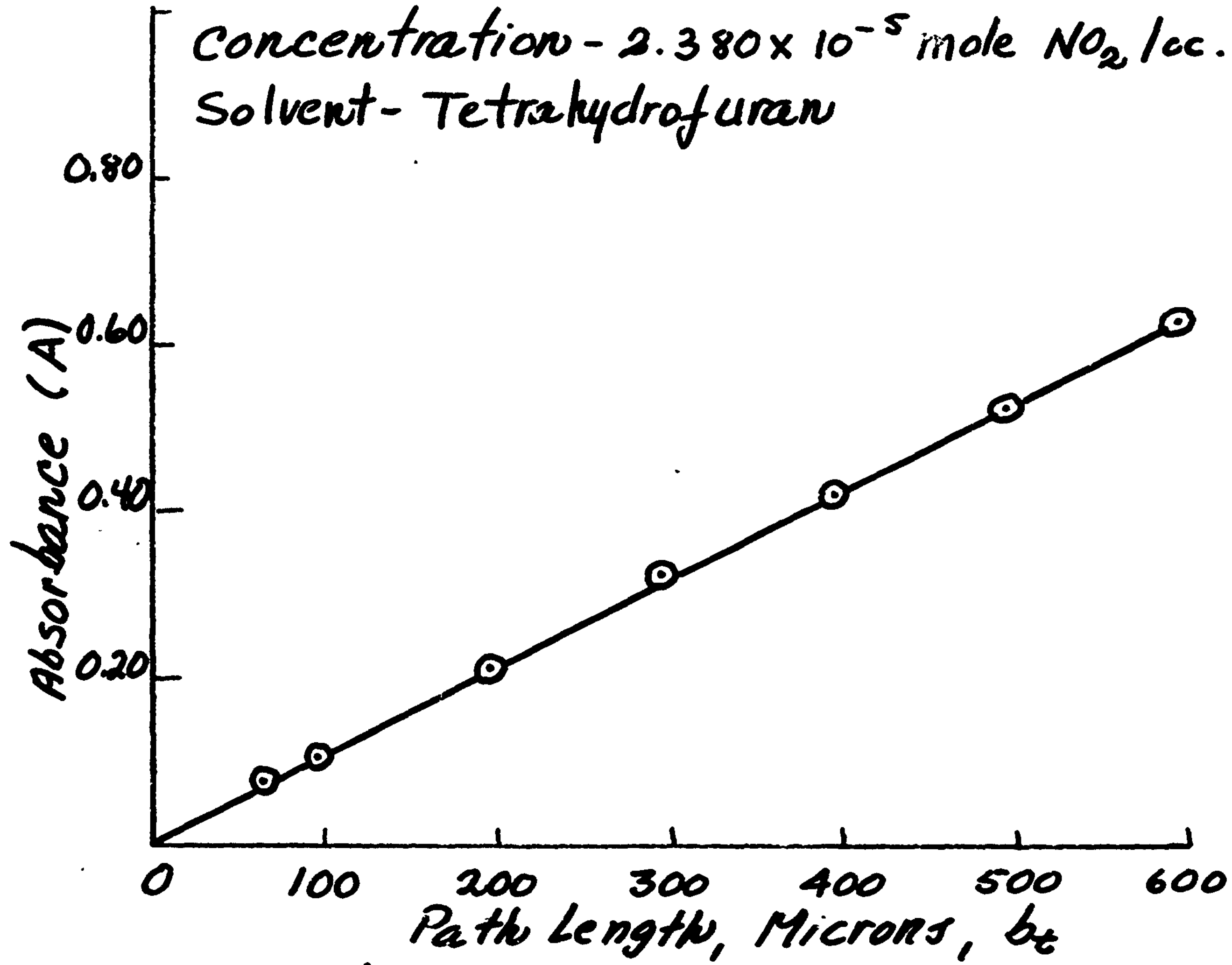

FIG. 20 Cellulose Nitrate (12.53%N) A vs b_t

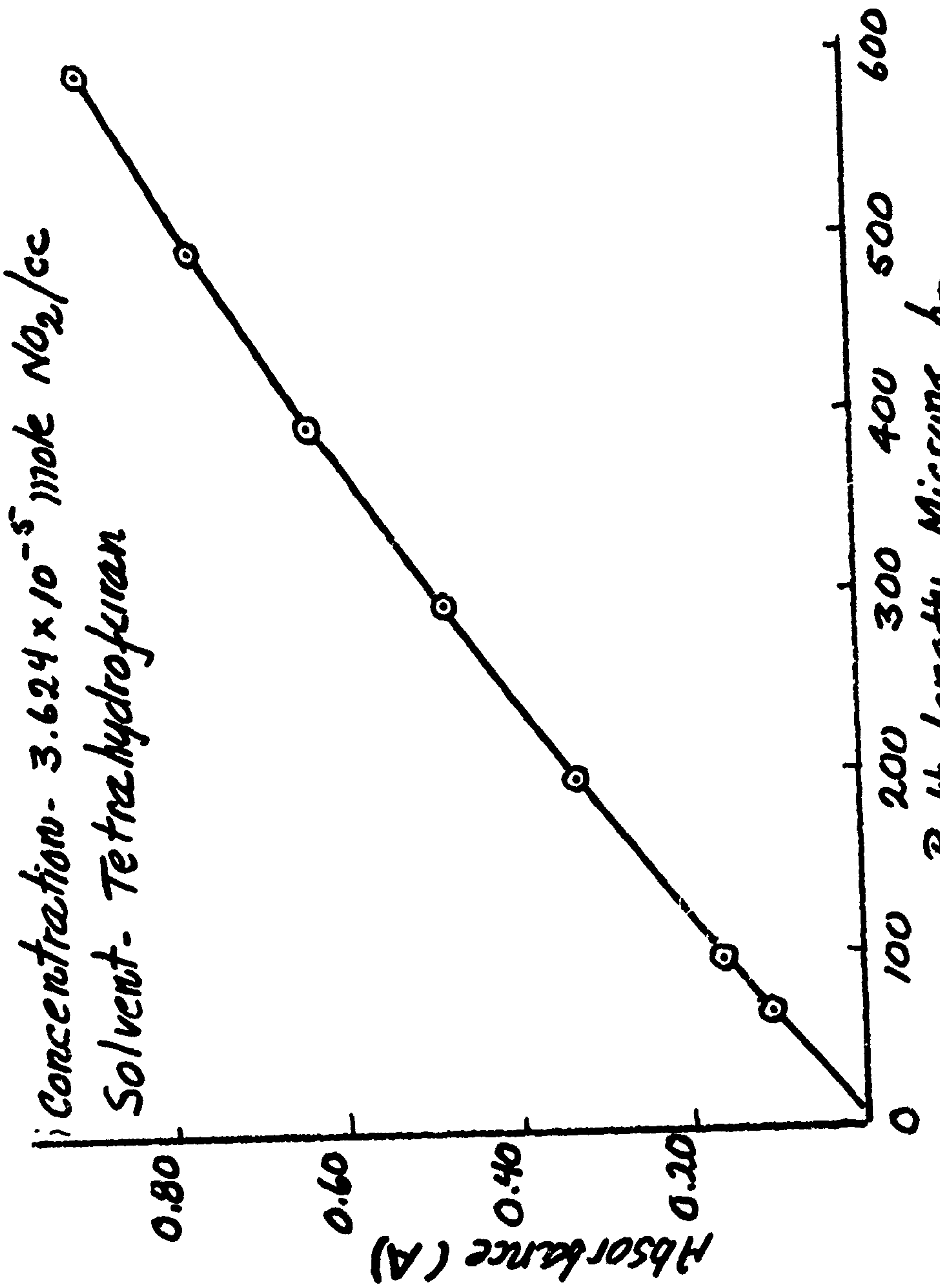

Fig. 21 Cellulose Nitrate (12.53% N) A vs b_t

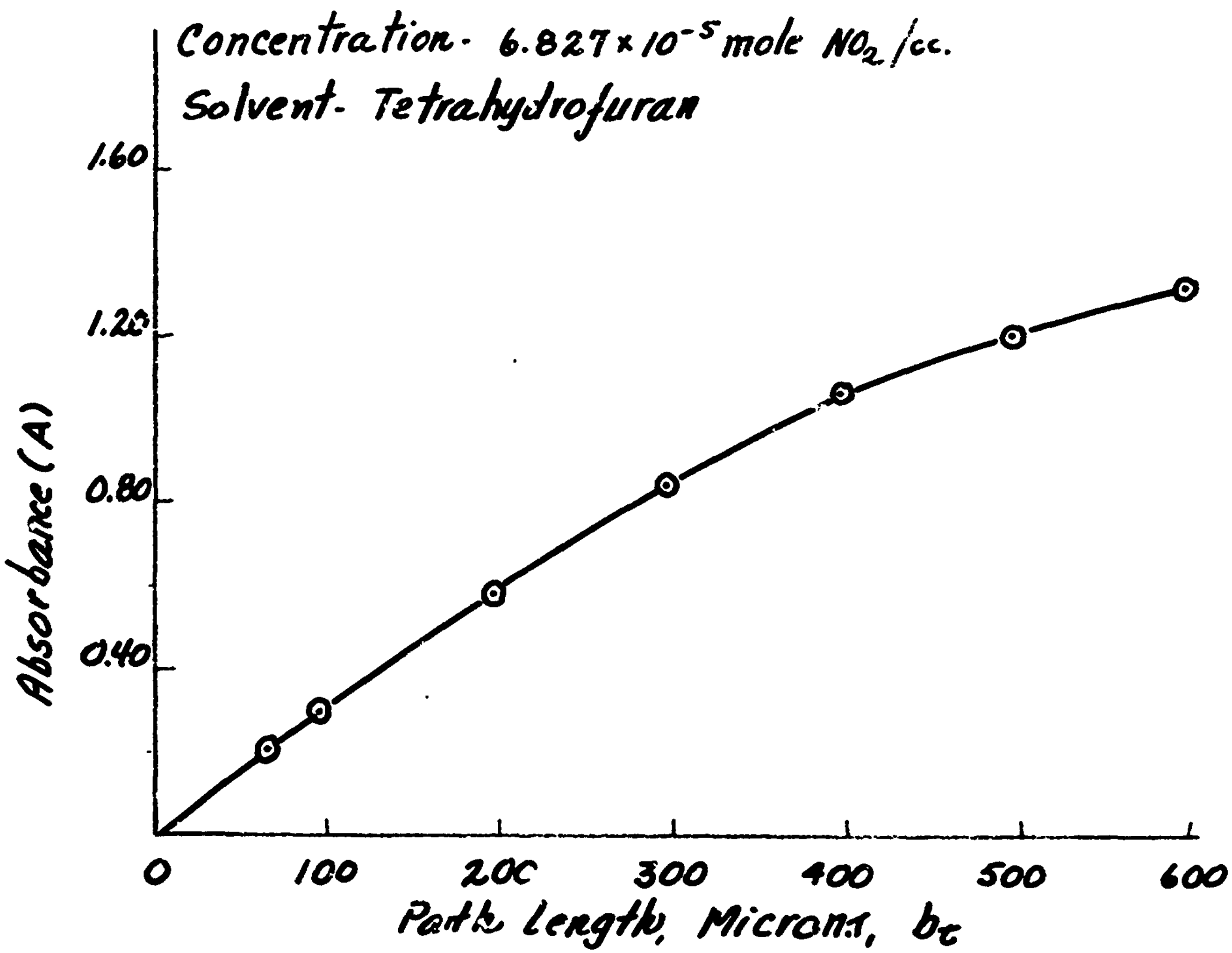

FIG. 22 Cellulose Nitrate (12.63 %N) A vs b_τ

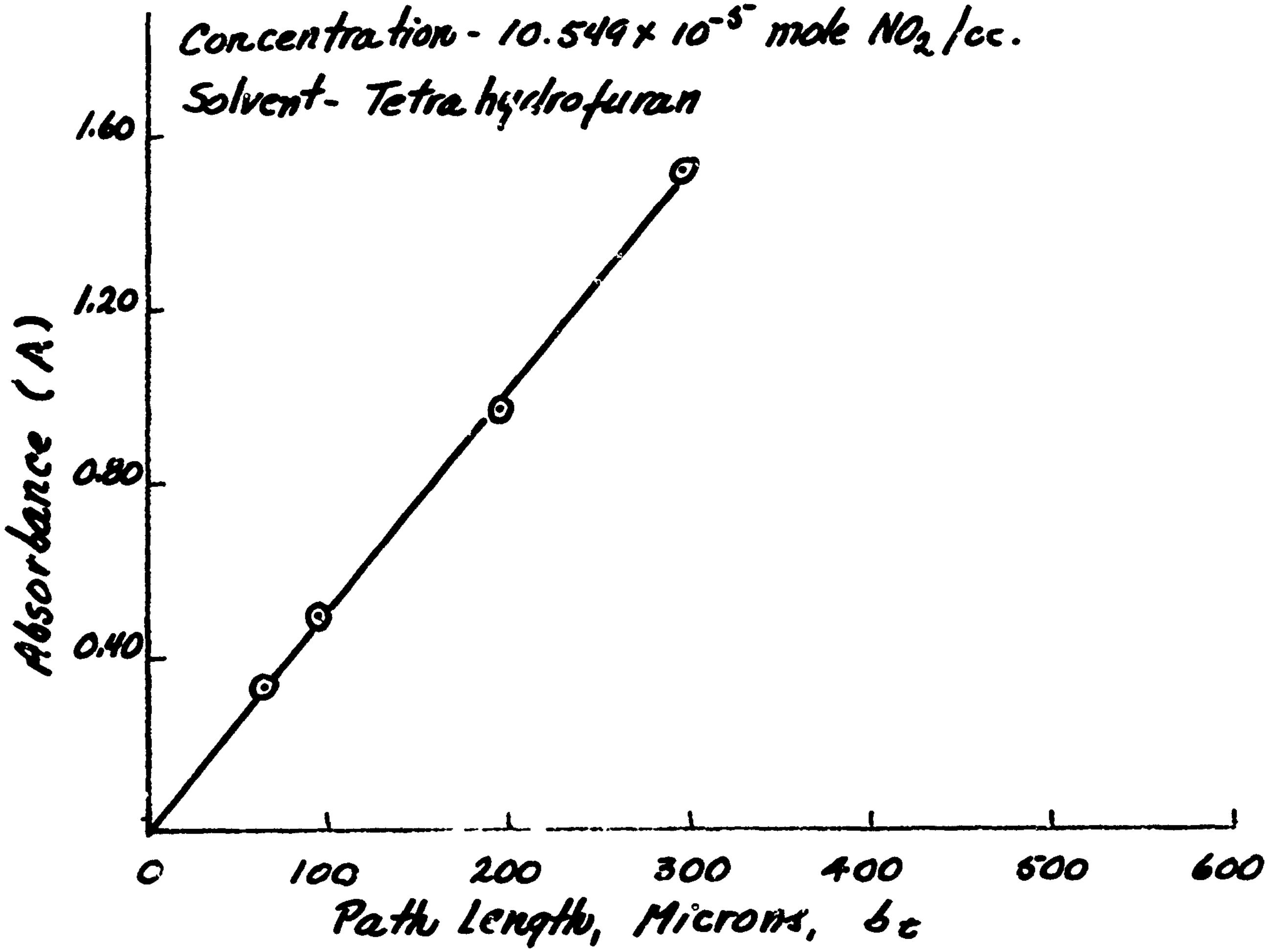

FIG. 23 Cellulose Nitrate (12.53 %N) A vs b_t

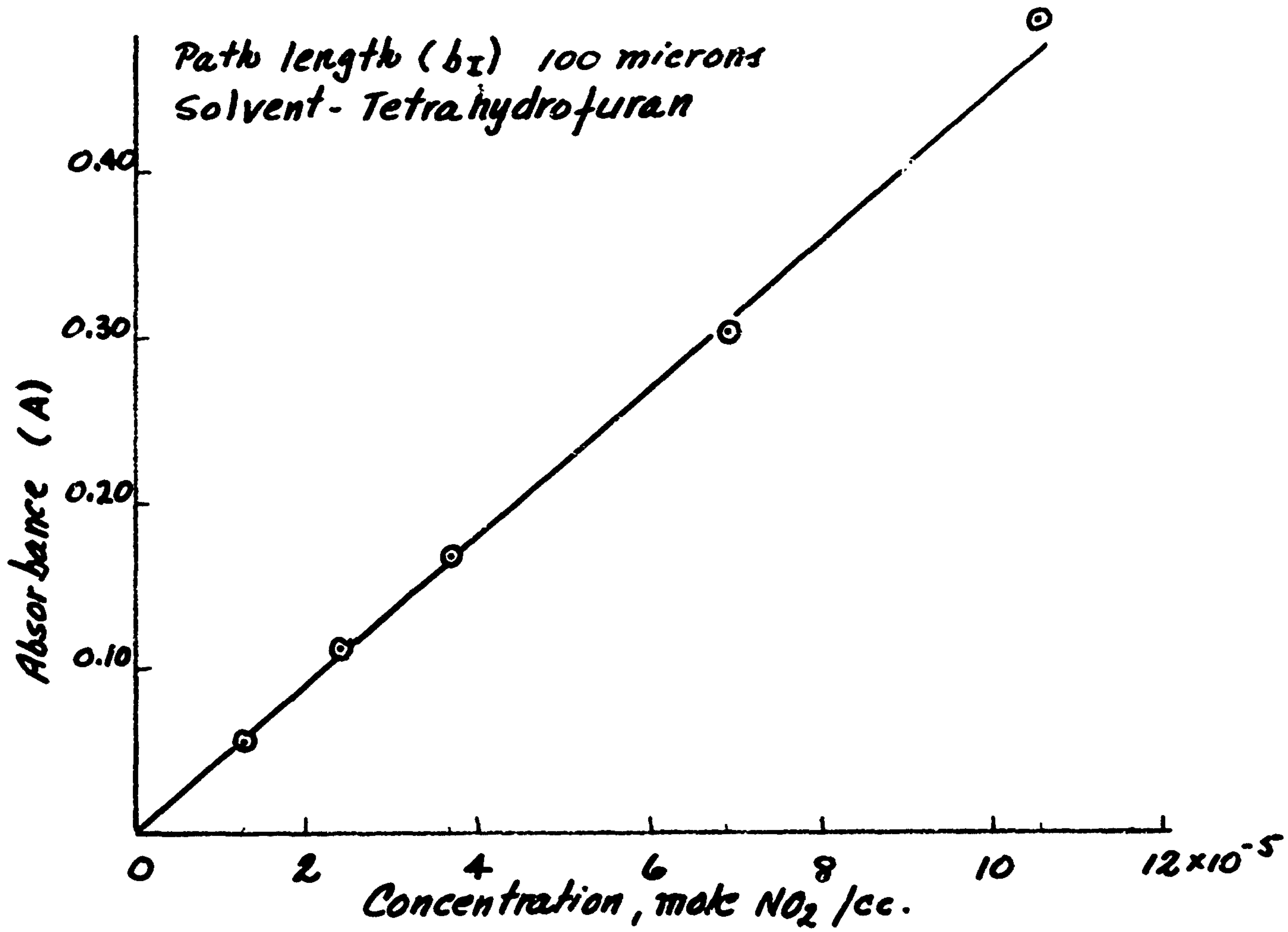

Fig. 24 Cellulose Nitrate (12.53% N) A vs Concentration.

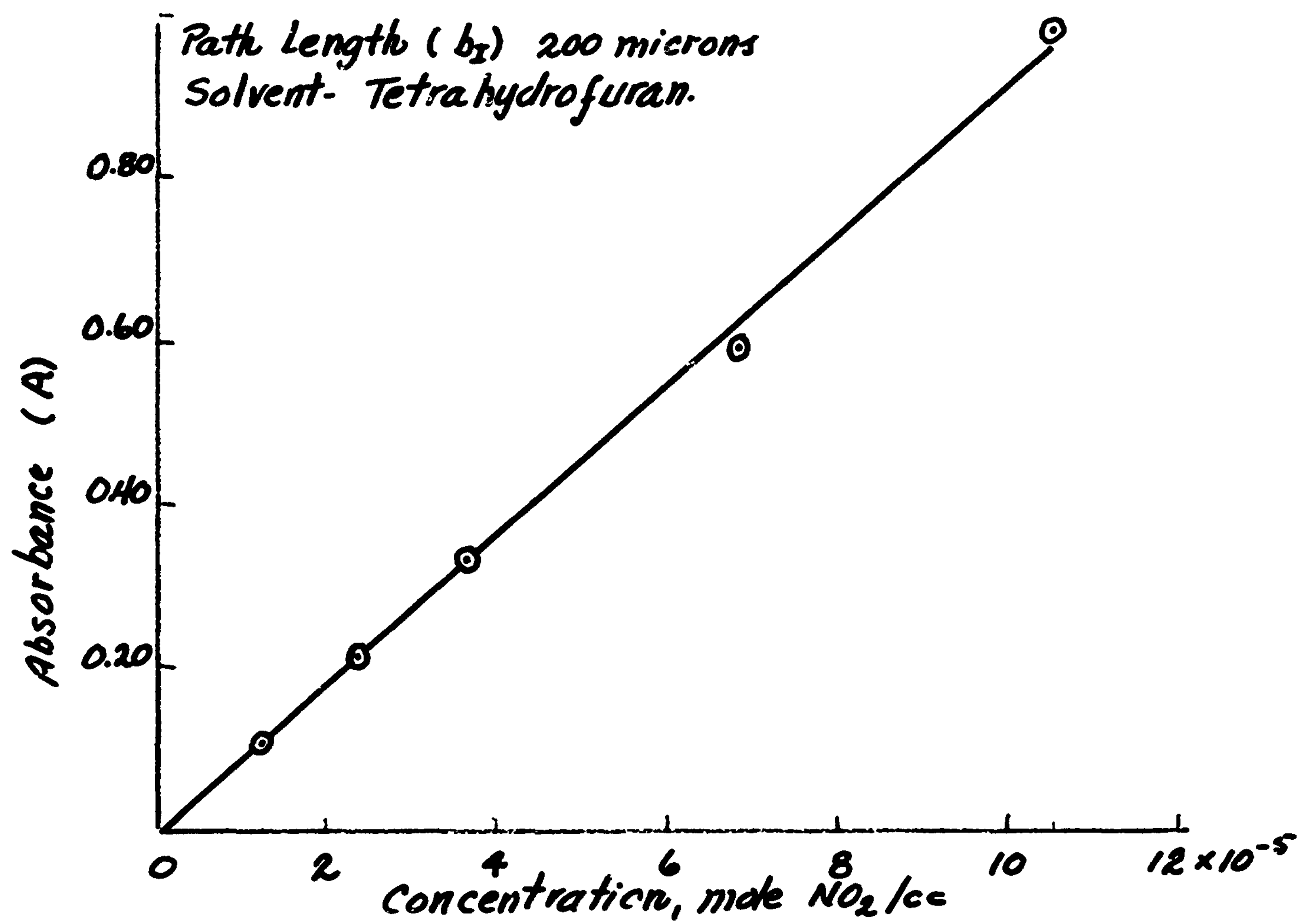

Fig. 25 Cellulose Nitrate (12.53%N) A vs Concentration.

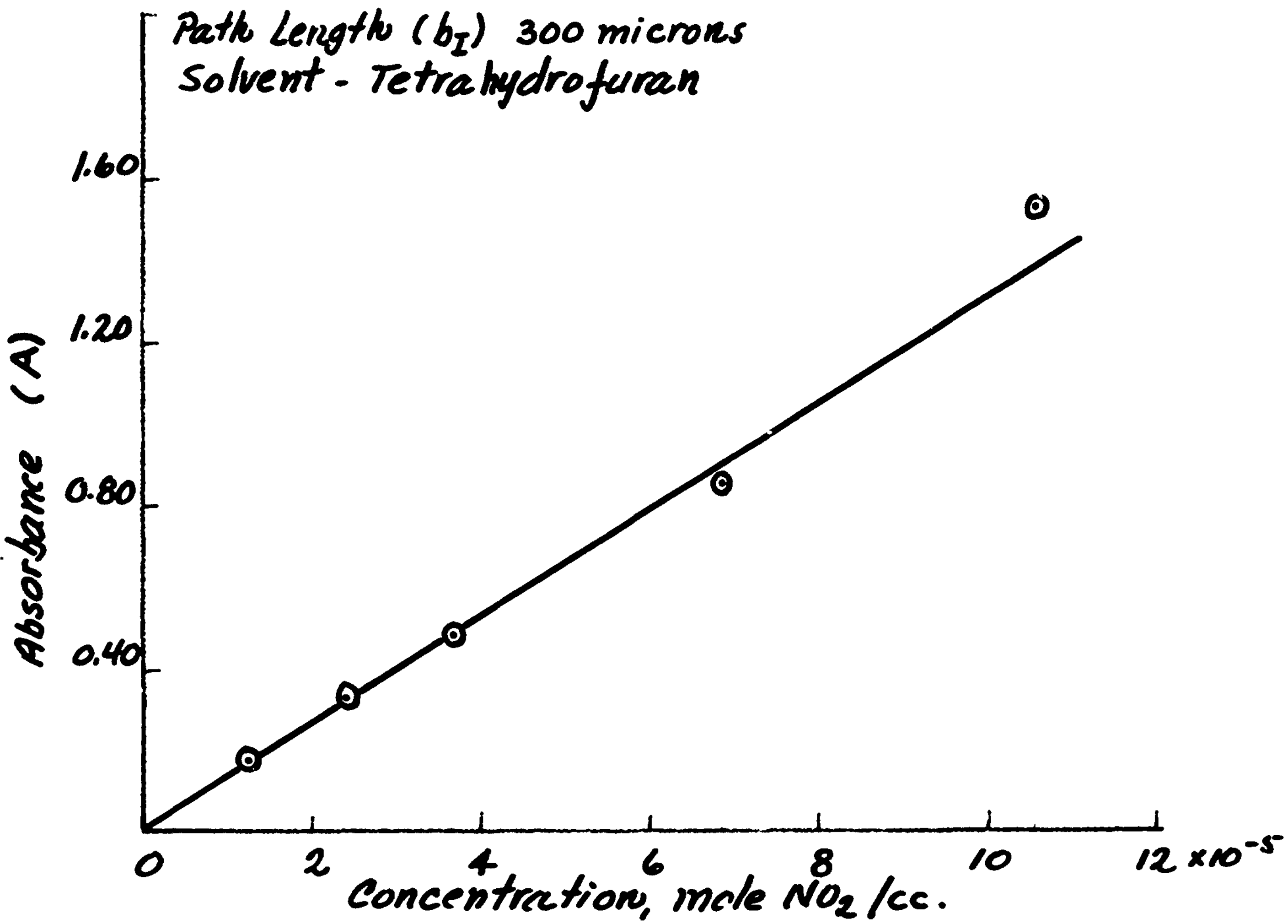

FIG. 26 Cellulose Nitrate (12.53% N) A vs Concentration.

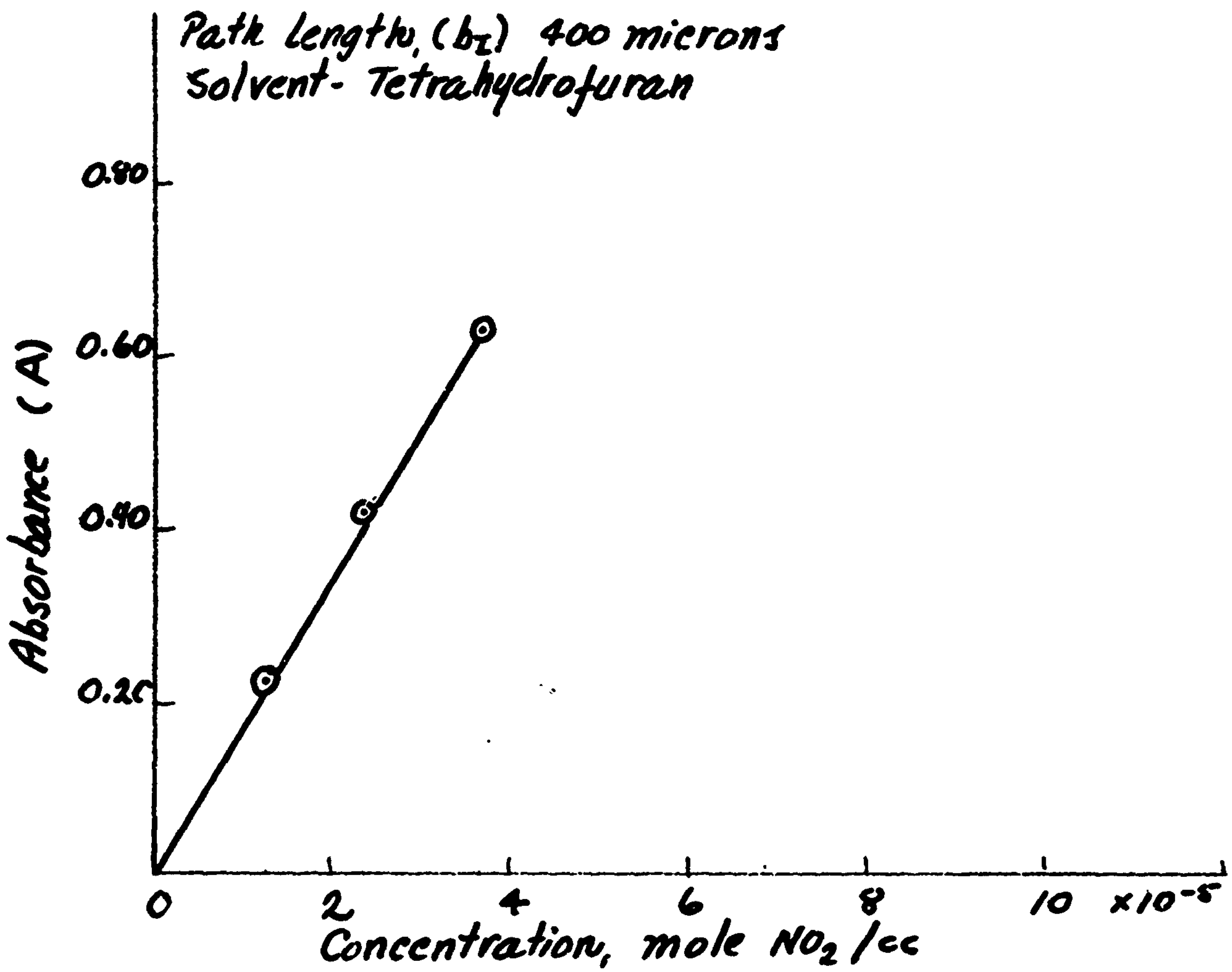

Fig. 27 Cellulose Nitrate (12.53%N) A vs Concentration.

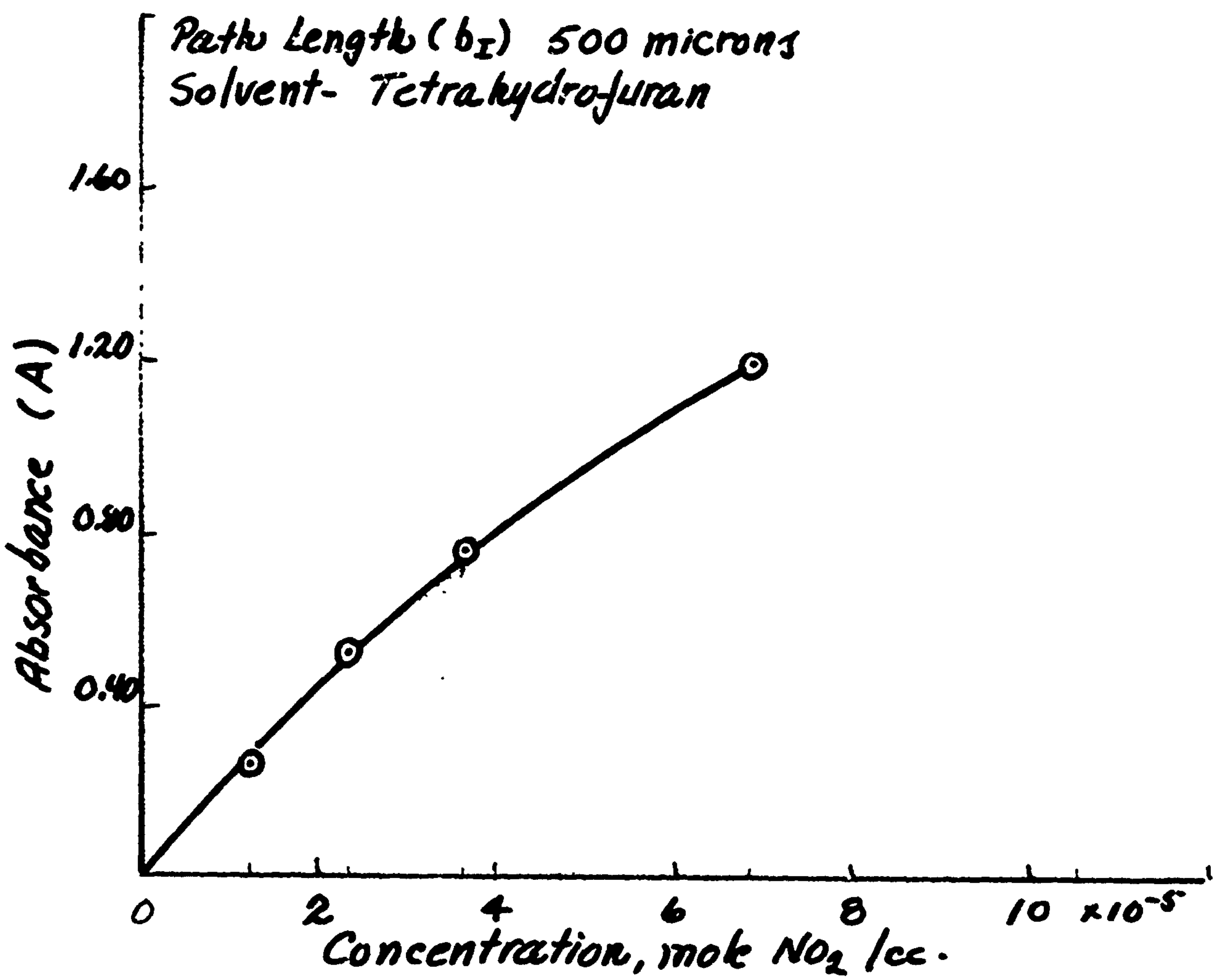

FIG. 28 Cellulose Nitrate (12.53 % N) A vs Concentration.

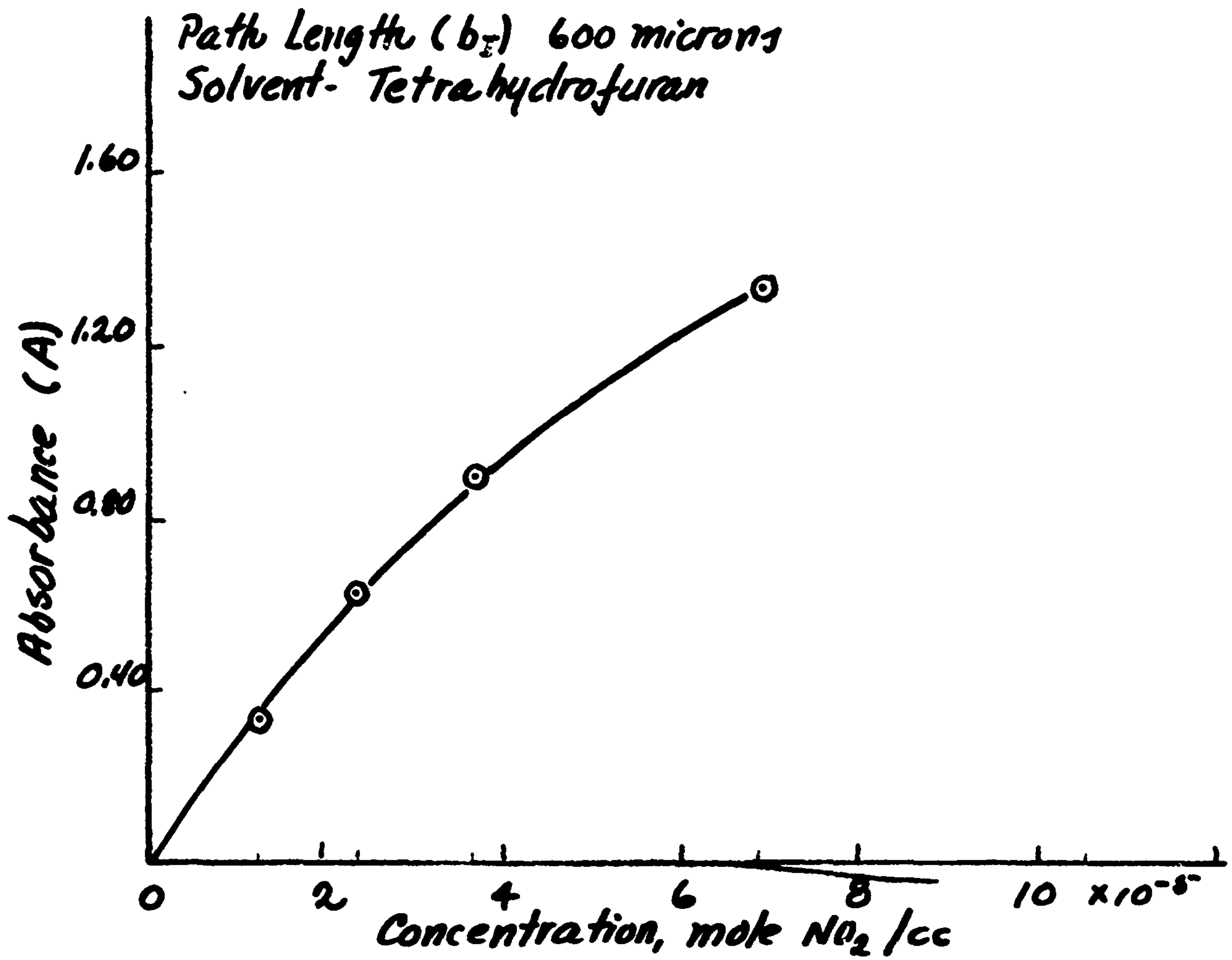

Fig. 29 Cellulose Nitrate (12.53%N) A vs Concentration.