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QUALITATIVE AND QUANTITATIVE ANALYSIS OF ENCLOSED ATMOSPHERE BY LIQUID CRYSTALS

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13. ABSTRACT

The development of a total liquid crystal system for trace contaminant detection in closed atmospheres has been designed, and quantitative information has been obtained for liquid crystals which respond to organic vapors. The vapors which have been detected are aromatic, aliphatic and chlorinated hydrocarbons. The electronic and vapor chamber design are described and preparation of liquid crystal materials is included. The theoretical and practical limitations of liquid crystals have been determined and compared with good agreement. A practical limitation of reversible organic detection was found as 50 parts per billion (ppb). Response curves for 32 organic solvents are included as an appendix for reference purposes. The measurement of diffusivity for organic vapors and liquid crystals was determined, and the effect was established as a bulk phenomenon which is completely reversible. Novel derivatives were made of 3β-carboxy-5-cholestene, which show interesting liquid crystalline properties.

Key Words: analytical chemistry, vapor detection, cholesterol, cholesteryl esters, 3β-carboxyl-5-cholestene, liquid crystals, cholesteric phase, vapor diffusion, organic vapor detection, diffusivity

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This technical report has been reviewed and is approved.

CLINTON L. HOLT, Colonel, USAF, MC
Commander
Aerospace Medical Research Laboratory

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SECTION I

INTRODUCTION

The cholesteric liquid crystal is highly colored when viewed with ambient lighting (ref. 1). If the intensity of reflected light is measured as a function of wavelength, the material will show a reflection maximum, which is approximately 200 Å wide in the green. The scattering peak can be easily measured with a monochrometer and a photocell. The color at any temperature is dependent upon the composition of the material. If the composition is changed by even a small amount, the color of the liquid crystal alters dramatically. In Figure 2, we illustrate the change caused by a 5 percent change in the proportion of cholesteryl chloride added to cholesteryl oleyl carbonate.

Since the measurement of wavelength is one of the most sensitive tools we have in chemical analysis and spectroscopy, we would expect a tremendous wavelength sensitivity for these materials. If we change the composition of a cholesteric liquid, we would then get a large change in color (ref. 2). If this change in composition was made by a volatile solvent, we could expect the solvent to be absorbed in the liquid crystal from the vapor phase, and thus form an equilibrium with the liquid crystal which would depend on Henry's law (ref. 3). In other words, if a cholesteric liquid crystal is exposed to an organic vapor such as benzene, we would expect some of the benzene to be dissolved in the liquid crystal system and, since the color of the liquid crystal system would then be a function of the total composition, there would be a shift in the color, depending on the effect of the benzene. The effect, as we shall see later, is found to be linear. Therefore, we could expect color (i.e. wavelength reflected) to change, depending on the concentration, in a linear manner. The concentration of benzene in the liquid crystal would depend upon Henry's law; that is, the concentration of the vapor in the material is equal to some constant times the concentration of the gas above the liquid crystal, if

$$c = kx$$

where c is the concentration in the liquid crystal, k is the Henry's law constant, and x is the concentration in the gas in the vapor phase. This is illustrated in Figure 1, where a continuing change of concentration is monitored by lines of color. This describes a bulk effect, and we should be careful to delineate a bulk effect from a surface effect. In our case, the gas molecule diffuses into the liquid crystal, changes its composition and, therefore, its color.

We have succeeded in showing that the color change is indeed a bulk effect by using thick films in which the color changes occur not only in lateral dimension but in depth, and a diffusion of gas into the liquid crystal can readily be seen. This would not be possible with a surface effect. See Figure 3 for the appearance of three cholesteric liquids which were used in gas sensing; data is particularly suited for discrimination or qualitative analysis.

The use of electronic monitoring allows us to measure the wavelength to a very high accuracy, and very small changes on the order of 0.1 Å will be readily visible.

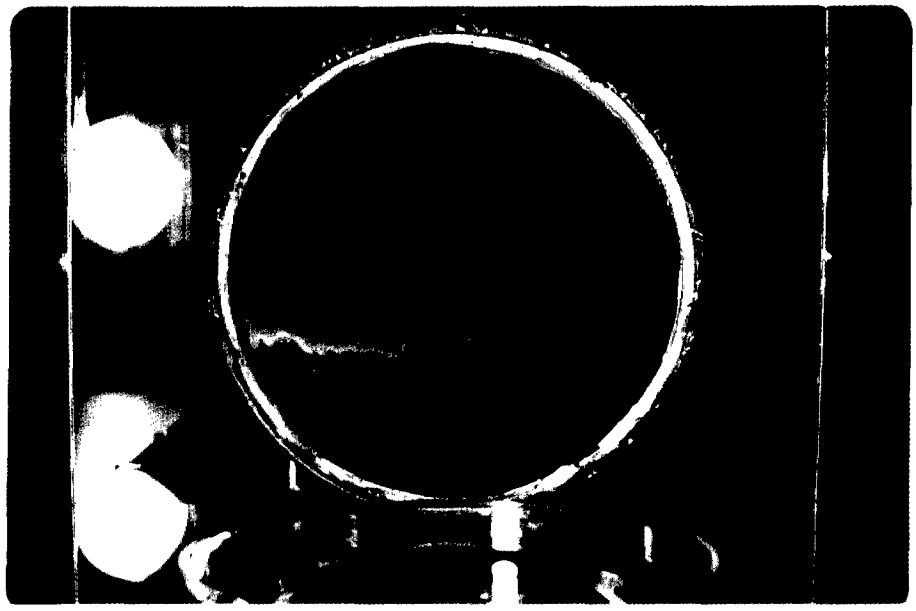
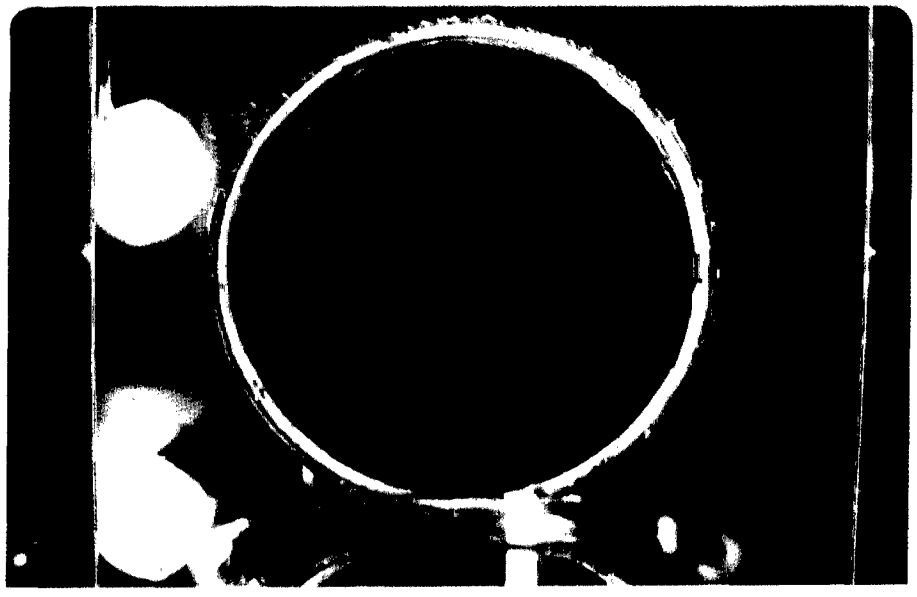


FIGURE 1

Chamber with chloroform vapor diffusing upward from a small container, showing the progression of the solvent level upward into the container after 1 minute (a) and 6 minutes (b). The color bands indicate concentration levels.



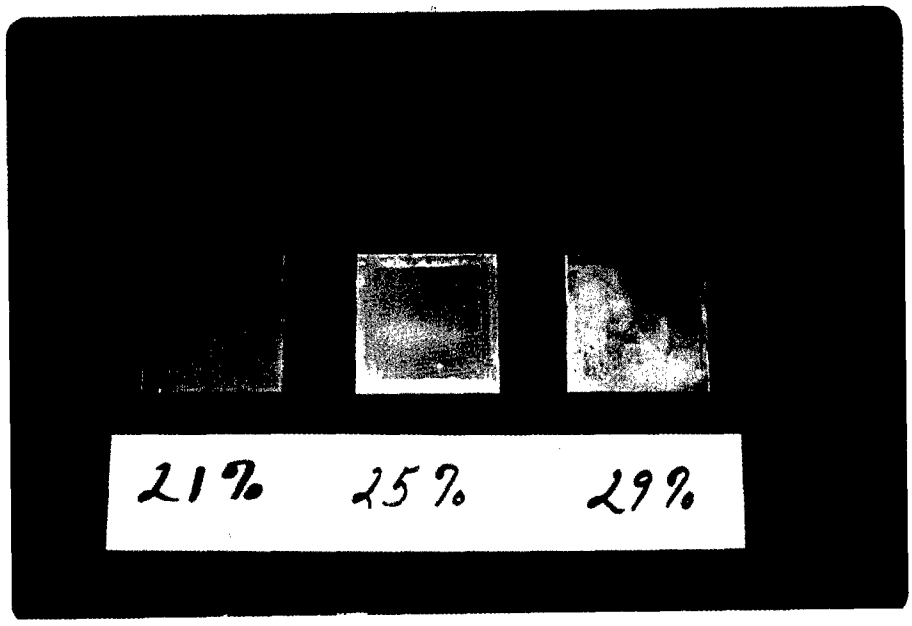


FIGURE 2

Three cholesteric mixtures which show a linear response with vapor concentration.

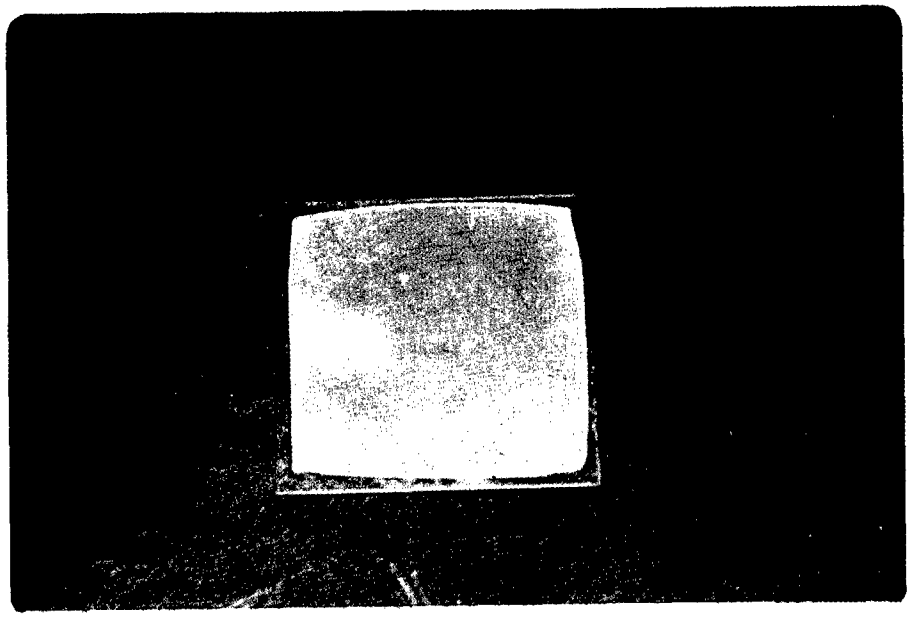


FIGURE 3

Diffusion of vapor between glass slides in a cholesteric liquid crystal. The red line indicates the penetration of chloroform into the liquid crystal.

SECTION II

APPARATUS

For this program we developed the instrumentation required for quantitative and qualitative measurements of color changes in liquid crystals as well as remote sensing of liquid crystals. One net result was that the electronic sensing of liquid crystals is much more effective than observation by eye. It allows a greater range of discrimination plus a greater range of quantitation.

The apparatus developed can be divided into three subgroups: (1) the controlled atmosphere chamber; (2) the temperature control; and (3) the light sensing system. In building the controlled atmosphere chamber, we developed two designs. The first design, shown in Figure 4, was with a 1-liter capacity bell jar which used the base plate of a Fisher filtrator. The base plate was sealed with a piece of neoprene sheet and was evacuated with a Welch pump. A liquid nitrogen cold trap was used to prevent back diffusion of fore-pump oil. Provision was made for using a light pipe to sense the color of a liquid crystal through the bell jar. Injection of solvent into the chamber was made through a standard septum arrangement similar to the type used with gas chromatography. To provide ourselves with a known concentration of vapor, the bell jar was evacuated and a known amount of solvent injected as a liquid into the vacuum.

The purpose for using a vacuum for our experiments was to allow rapid diffusion of the vapor throughout the volume of the chamber. If a solvent such as chloroform is injected into the unevacuated chamber, it must diffuse against the volume of air within the chamber. This is a relatively slow process so that final concentration build-up requires several hours of equilibration. We found that we could inject the solvent in vacuum, allow it to equilibrate, add air, and not change our reading from that before evacuation. Therefore, we were valid in assuming that the presence of gases which did not react with the liquid crystal, did not affect the basic reading of concentration. We, therefore, adopted a procedure of pumping the chamber, injecting the solvent, and then making our measurement. This allowed us to measure the wavelength of maximum scattering as a function of concentration without re-evacuating the bell jar for each new concentration.

We found this system to be inadequate, however, particularly for materials with high solubility, such as chlorobenzene. Apparently the chlorobenzene would be very rapidly absorbed by the neoprene rubber and would give false readings. Therefore, it was decided to build a somewhat larger chamber which would decrease the surface to volume ratio and to use as little organic material as possible to prevent the absorption of organic solvents.

To do this, we used a 12-inch vacuum chamber ring, with a 12-inch-diameter by 3-inch-tall glass cylinder, and a 12-inch-diameter by 1-inch-thick glass plate. This assembly was sealed by neoprene gaskets and placed on a stainless steel base plate. The vacuum chamber ring has eight ports which can be used for vacuum feed-throughs. We utilized one for pumping, a second for electrical feedthroughs, a third for gas inlet, and the fourth for a septum. The extra ports were sealed. The septum we utilized was manufactured for use in a vapor-phase chromatography apparatus. Injection was made through replaceable rubber discs. The chamber was checked to 10^{-4} torr and found operational. The construction of the apparatus is shown in Figures 5 through 8 and a block diagram is shown in Figure 9.

The temperature control system was developed to allow close temperature control of the sample with simplified circuitry. For a temperature control element, we used a 1-watt Peltier cooling device fastened to an aluminum heat sink. The sample holder was an aluminum block fastened to the top of the Peltier device, into which was inserted various temperature-measuring probes. For our purpose, we used both a thermocouple and a thermolinear thermistor probe. The thermocouple was used only to check the calibration of the thermolinear probe, which was found to be linear within .2°C and reproducible to within $\pm$.01°C. By using a linear wirewound potentiometer, properly calibrated, we were able to develop a direct-reading temperature control.

The circuit of the temperature control system is shown in Figure 10. The temperature is sensed by the thermolinear probe which is part of a bridge circuit which develops an error signal proportional to the temperature imbalance. The error signal is amplified by the data amplifier and fed to a power amplifier, which in turn drives the Peltier cooler. Since

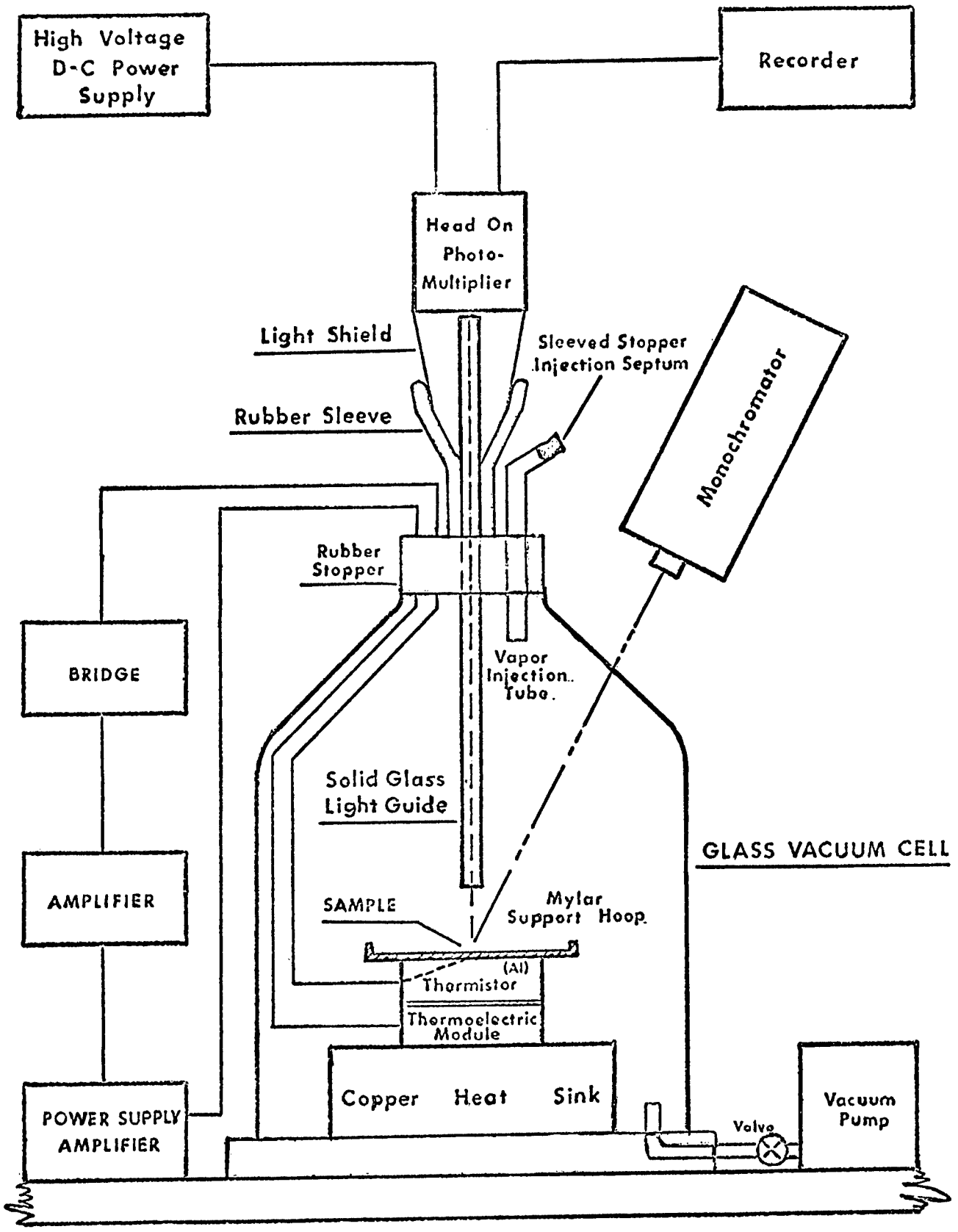


FIGURE 4

The first vapor detection apparatus designed for quantitation of the response of liquid crystals to vapors.

this uses a direct error signal which is amplified and fed back into the Peltier cooler, the system achieves proportional control. The gain on the system is set so that no oscillations in temperature occur. This can be determined by monitoring the current input to the Peltier cooler. When the Peltier cooler no longer draws current, we assume that the equilibrium temperature has been reached and is being controlled.

Two modifications of this circuit were used, one using standard amplifier modules. The data amplifier was the 520 Hewlett-Packard 2470. The power amplifier was the Hewlett-Packard 6824A. This gave us considerable flexibility at arriving at the design parameters for a finished controller. The second controller was built from integrated circuits to reduce size and cost and to show that it could be built within a reasonable size package. The resulting circuit is shown in Figure 10. This circuit had very high stability and controlled temperature to $\pm.1°C$ for unlimited periods.

The third system was the electro-optical liquid crystal monitoring system. For a light source, we used a Bausch & Lomb high-intensity monochrometer with a tungsten source. The tungsten source was used to reduce fluctuations due to AC current. The high-intensity monochrometer illuminated the film which was on the temperature-controlled sample holder. The reflected light was monitored by a light pipe which was connected to a silicon photodetector. The silicon photodetector output was re-fed to a recorder. The output could be monitored either as a function of wavelength by adjusting the input wavelength of the monochrometer or as a function of time at a fixed wavelength of illumination. A Mosely X-Y Recorder was used for output monitoring.

An earlier configuration of the detector was to use a photomultiplier with an S20 surface. The S20 surface has a wide spectral response. It was found that the signal from the liquid crystal, however, was sufficiently strong to avoid use of a photomultiplier which uses high voltage. The use of a silicon detector allows the matching with standard solid state circuitry without the use of high voltage. This also allowed the sensor to be enclosed within the controlled atmosphere chamber, making the pickup much simpler.

The final model for gas detection resulted in a completely transistorized sensor unit and temperature control which could be extremely small in size. The largest single component and the largest power consumption is the light source, in our case the Bausch & Lomb high-intensity monochrometer, which for size reduction could be replaced by interference filters and a small tungsten lamp or a gas discharge tube.

The apparatus as designed is apparently completely suitable for remote monitoring of the color of cholesteric liquid crystals. The small size of silicon detectors also makes it possible to use multiple detector array to sense the color of different liquid crystals. Thus, using available detectors and cholesteric liquids, it should be possible to build 9 x 9 arrays of liquid crystals on sensors within a 1 sq. cm x 4 cm volume. The illumination of such an array could be made by a single light source.

Other techniques which we used and appear to be practical are the bifurcated light pipes which allow remote positioning of both the light source and the detector array.

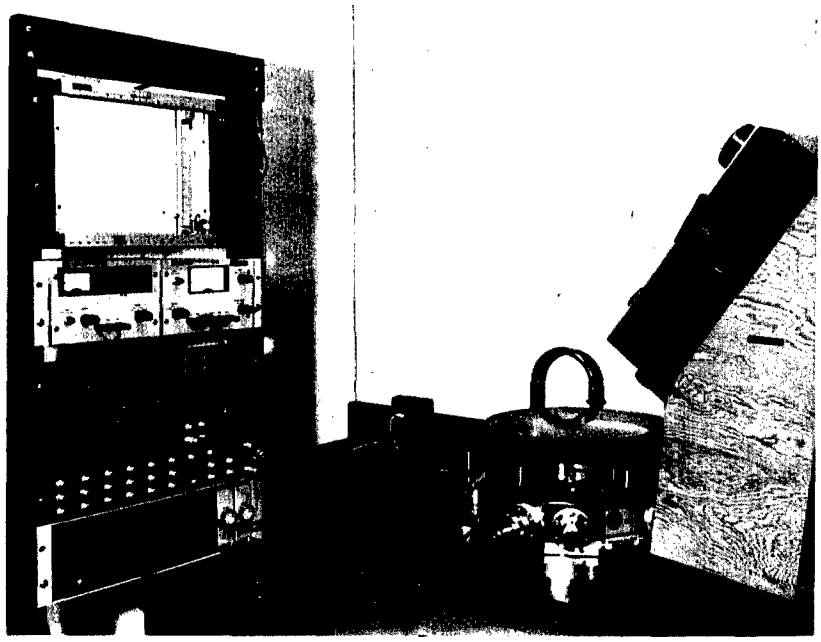


FIGURE 5

The apparatus used to determine the quantitative response of liquid crystals to vapors.

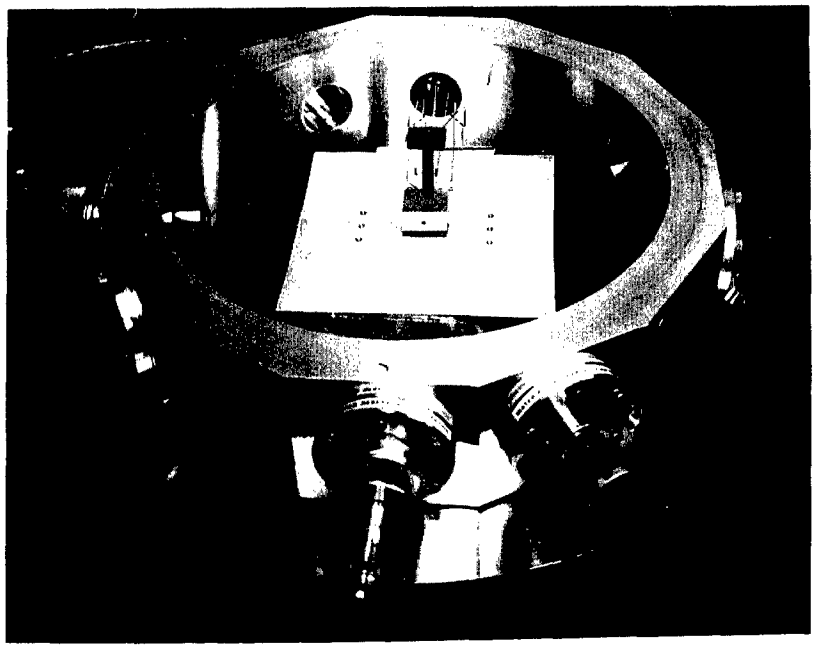


FIGURE 6

The interior of the controlled atmosphere chamber showing the Peltier cooling block and the light pipe with the silicon detector. In the front quadrant is shown the injection septum.

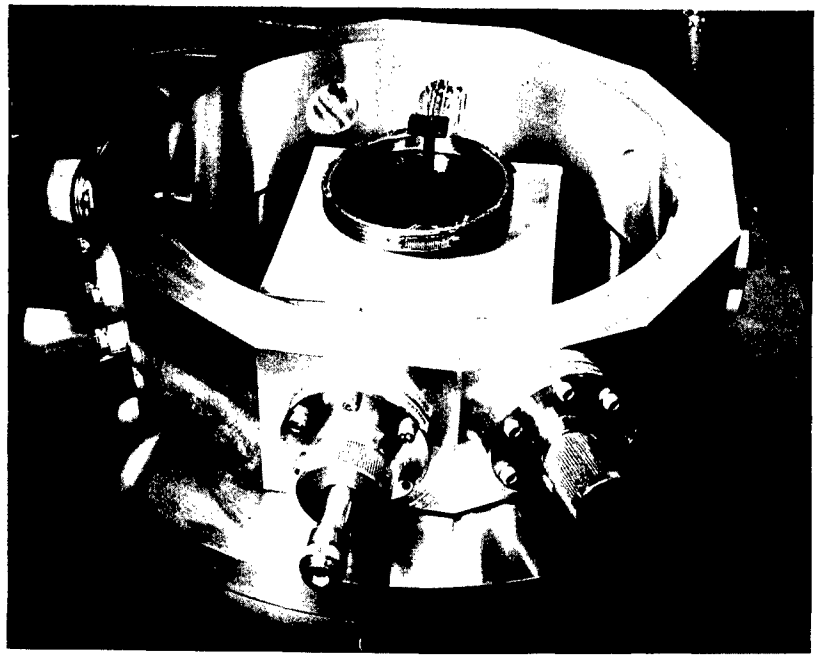


FIGURE 7

The interior of the chamber with the liquid crystal holder in place on the Peltier cooling device.

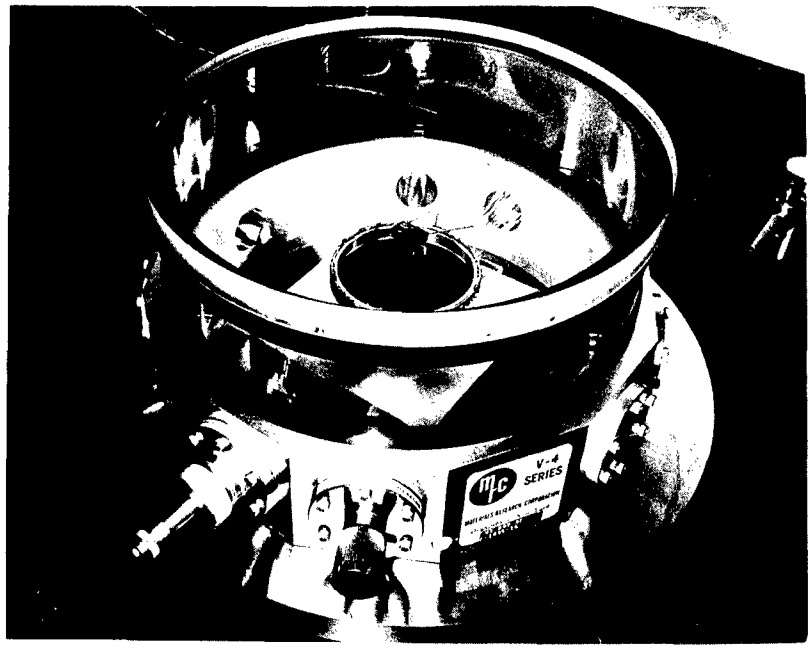


FIGURE 8

The assembled chamber.

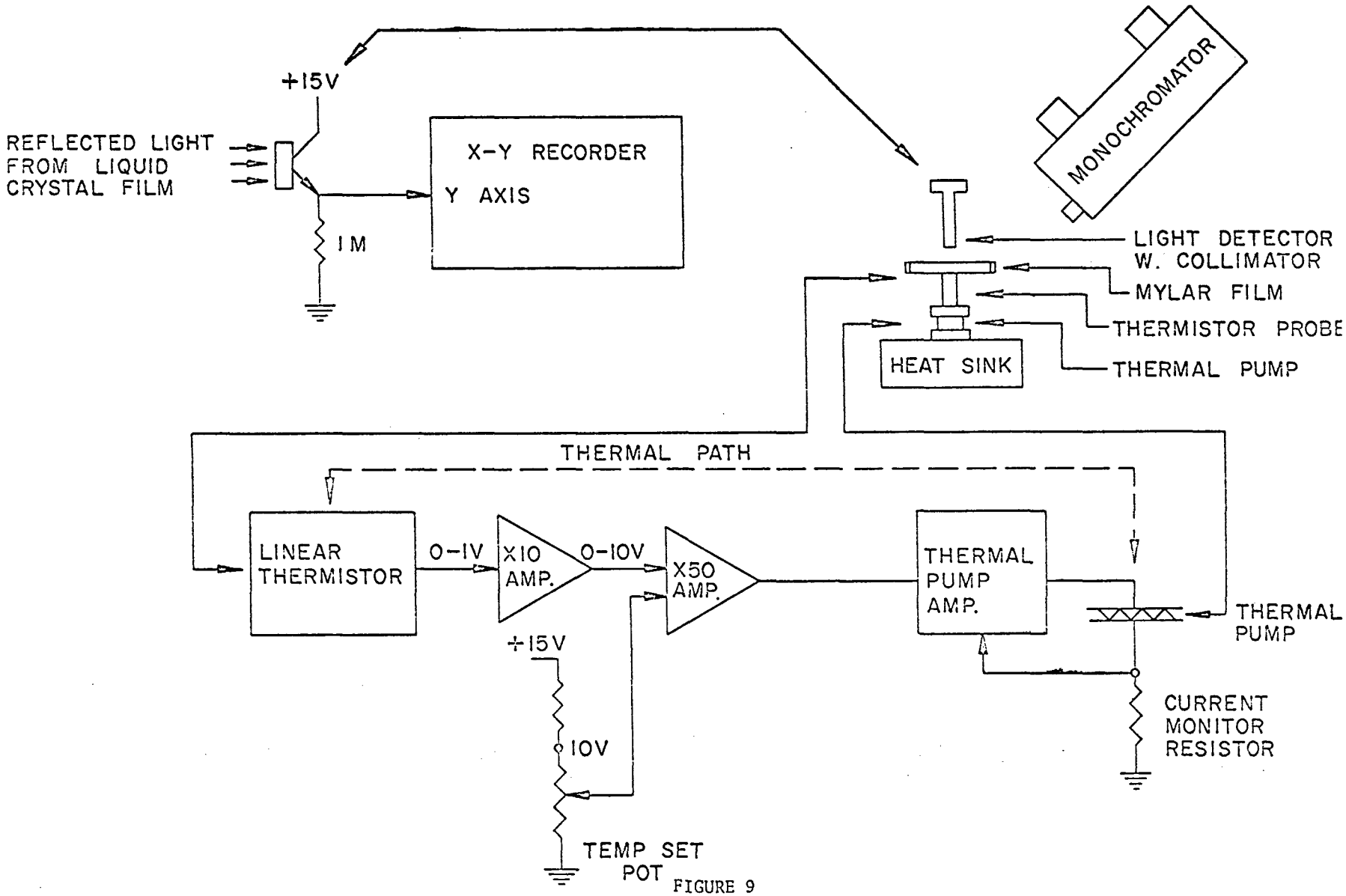
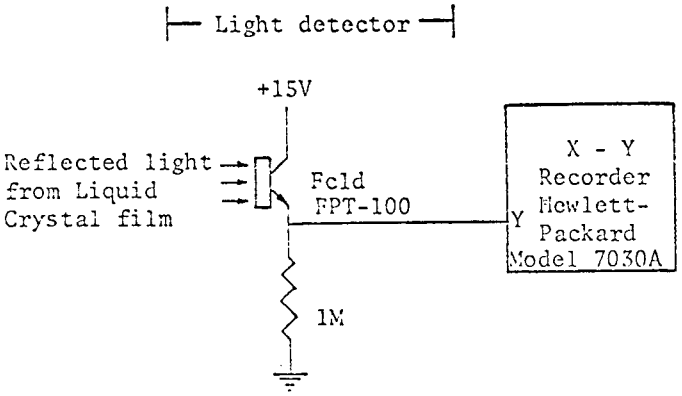


FIGURE 9

The block diagram of the currently used vapor detection device.



NOTES:

1. All resistors 1/4 w. 5% unless otherwise stated.
2. All Op Amps Burr-Brown #3077/12C.
3. Manufacturer abbreviations: YSI, Yellow Springs Instrument; PPP, Phipps Precision Products Co.; MOT, Motorola; Al, Allied Radio Corp.; Fcld, Fairchild.
4. Power transistors, 2N4913 and 4904 must each be heat sink mounted for 15 watt dissipation.
5. The thermal pump must be heat.sink mounted for 25 watt dissipation.

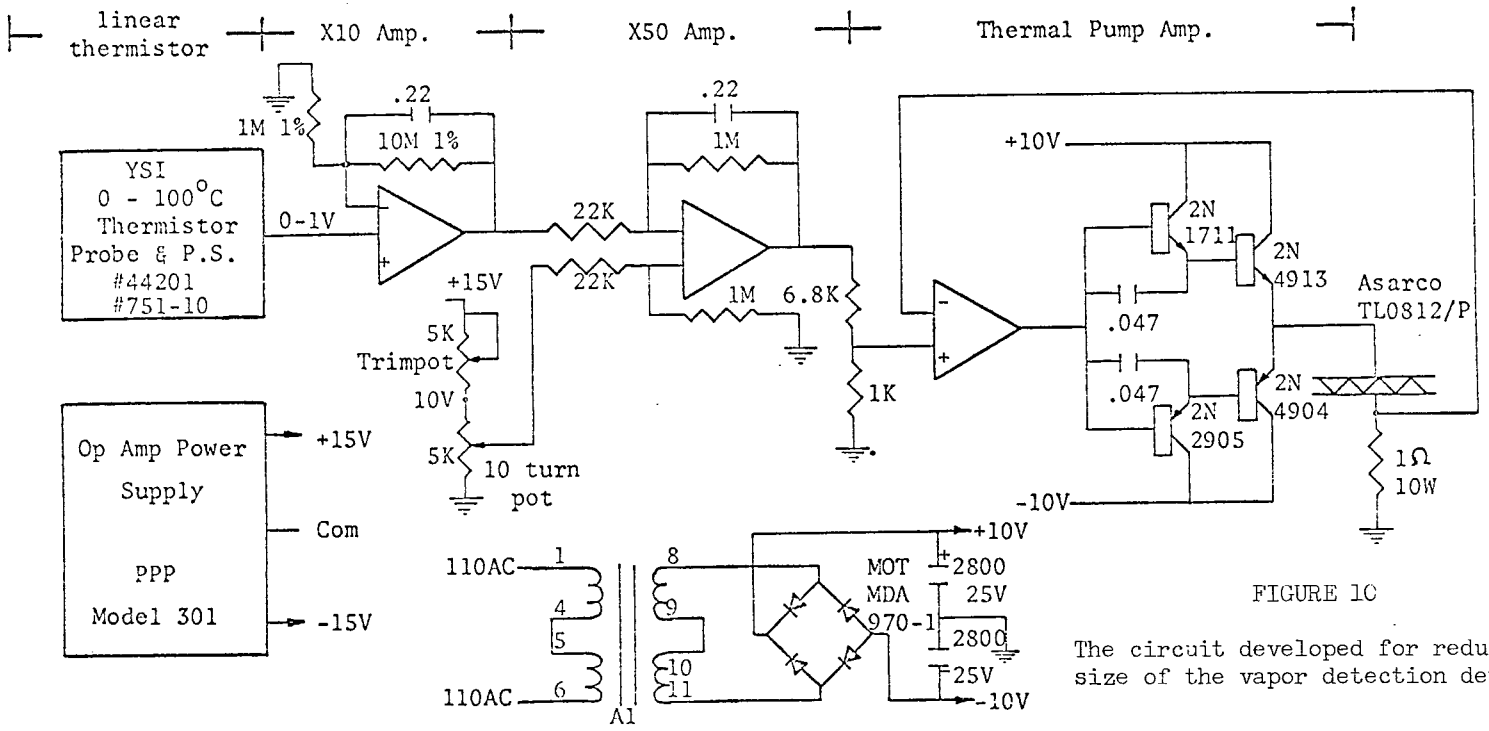


FIGURE 10

The circuit developed for reduction in size of the vapor detection device.

SECTION III

EXPERIMENTAL

PREPARATION OF THE LIQUID CRYSTAL

The sample for gas sensing is prepared on a mylar surface. The background is black to reduce scattering. The mylar surface is prepared by stretching 12 micron mylar in a standard embroidery hoop. The liquid crystal is placed on the hoop by applying one drop of a solution of 10% cholesterol esters in 90% petroleum ether. This results in a film which contains .08 grams of liquid crystal and has a thickness of approximately 10 microns. This is the optimum thickness and concentration.

After the film has been prepared in this manner, the hoop is placed on the Peltier cooler (see Figure 7). The detection chamber is then assembled as shown in Figure 5 and the solvent of interest is injected through the septum. This has given better results than dilution techniques. Generally, the measurements are repeated on each film three to four times to insure reproducibility and reversibility.

One of the difficulties encountered is the backstreaming of oil fumes from the forepump. Even in the presence of a nitrogen trap, this is appreciable if the pump is left on for more than 30 to 40 minutes. If the film is, however, kept in a closed chamber, the lifetime appears to be nearly indefinite. Tests of this type show that the film will remain for at least six weeks in the active form with no evidence of deterioration.

The simplicity of operation which we have achieved with this device allows us to look at the solvent response from a large number of liquid crystals and gas vapors.

EXPERIMENTAL AND RESULTS

The previously described apparatus was used to accumulate data on the response of a number of liquid crystal systems. Since the number of materials which exhibit the cholesteric phase and respond to various vapors is very large, this cannot represent a complete study. The mixtures of cholesteryl chloride (CCl) with cholesteryl oleyl carbonate (OCC) and cholesteryl nonanoate (CN) were chosen for study, primarily because the response to that vapor was nearly linear and the temperature sensitivity was extremely low. Although numerous other systems were tested, no complete study was made.

The advantage of a linear response to concentration makes direct comparison of results possible. The response of the liquid crystals to a number of isomeric and a number of halogenated compounds was studied. The sensitivity depends on vapor pressure, since this is directly related to Henry's Law constant. The response also depends on the dipole moment of the molecule and the tendency for it to hydrogen bond. In the case of the dipole moment, either a decrease or an increase may result. For materials which tend to hydrogen bond, there is generally a decrease in sensitivity. Tables I through V summarize the results with a number of homologous series of vapors and also with several liquid crystals.

Comparing the slopes shows that each individual material is different and will depend on its composition. Of particular interest is the result with the ortho-, meta-, and para-substituted xylenes. Here we have a case where positional substitution of methyl groups on an aromatic ring makes disproportionately large changes in slope (see Figure 11). This sensor could be used to measure directly the concentrations of these materials: and if concentrations were known, a qualitative analysis of the materials could be made.

The second very interesting group is the chloro-substituted methanes. Not only does the slope change from various chlorinated compounds, but the difference in the slope between different materials is quite marked. For instance, the 24% cholesteryl chloride material has a steeper slope for the dichloromethane than the carbon tetrachloride. This difference might be attributed to the dipole moment. The chloroform, however, has the most marked effect, having a slope of 12.07×10^4 μm liter/mole.

The 26% cholesteryl chloride, however, shows a marked difference. The material is more sensitive to chloroform than to carbon tetrachloride than to dichloromethane, and there is a net increase in slope. Again, the chloroform has a much steeper slope than either the carbon tetrachloride or the dichloromethane. In this case, there is no correla-

TABLE I

LIQUID CRYSTAL MIXTURE: 76% (60-40, OCC-CN), 24% CCl, 18°C

Solvents	*B. P.* °C	*Vapor Pressure Torr*	*Slope* $\frac{(m\mu)\ liter}{moles\ x\ 10^{-4}}$
I. CHLORINATED METHANES			
a. Dichloromethane	40.1	351.2	3.50
b. Chloroform	61.3	171.6	13.02
c. Carbon Tetrachloride	76.8	89.9	3.16
II. AROMATICS			
a. Benzene	80.1	92.68	3.225
b. Toluene	110.6	19.53	11.63
c. o-Xylene	144.4	4.341	39.47
d. m-Xylene	139.1	5.524	26.315
e. p-Xylene	138.1	5.695	22.22
f. Fluorobenzene	84.8	57.73	6.185
g. Chlorobenzene	132.0	7.65	44.44
III. HYDROCARBONS			
a. n-Hexane	69.0	109.3	0.0
b. Cyclohexane	81.4	66.53	2.95
c. Methylcyclohexane	100.3	30.3	4.54
d. Cyclohexene	83.0	62.03	6.64
IV. KETONES			
a. Acetone	56.5	200.00	1.12
b. 2-Butanone	79.6	168.0	4.85
c. 2-Pentanone	101.7	71.41	8.46
d. 3-Methyl-2-butanone	93.0	28.62	6.23
V. ALCOHOLS			
a. Methanol	64.5	85.1	0.96
b. Ethanol	78.5	38.11	1.59
c. n-Propanol	97.2	14.05	6.10
d. n-Butanol	117.7	4.51	14.00
e. Iso-Propanol	82.3	31.13	3.33
f. 2-Butanol	100.0	12.16	1.10
VI. ESTERS			
a. Methyl Acetate	57.1	162.9	.44
b. Ethyl Acetate	77.2	70.26	2.14
c. Propyl Acetate	101.6	24.34	4.62
d. Methyl Propionate	79.9	62.49	2.62
e. Methyl Butyrate	102.3	23.62	6.21
f. Ethyl Propionate	99.1	27.1	4.20
g. Isopropyl Acetate	89.0	48.52	4.24
h. Methyl Isobutyrate	92.6	41.71	4.17

TABLE II

LIQUID CRYSTAL MIXTURE: 74% (60-40, OCC-CN), 26% CCl, 18°C

Solvents	*B. P.* °C	*Vapor Pressure Torr*	*Slope* $\frac{(m\mu)\ liter}{moles \times 10^{-4}}$
I. CHLORINATED METHANES			
a. Dichloromethane	40.1	351.2	3.47
b. Chloroform	61.3	171.6	17.50
c. Carbon Tetrachloride	76.8	89.9	4.74
II. AROMATICS			
a. Benzene	80.1	92.68	5.16
b. o-Xylene	144.4	4.341	63.64
c. m-Xylene	139.1	5.524	33.33
d. p-Xylene	138.4	5.695	26.31
III. HYDROCARBONS			
a. n-Hexane	69.0	109.3	0.0
b. Cyclohexane	81.4	66.53	2.96
c. n-Nonane	150.8	8.37	—24.40
IV. ALCOHOLS			
a. Ethanol	78.5	38.11	1.91
V. ESTERS			
a. Ethyl Acetate	77.2	70.26	2.67

LIQUID CRYSTAL MIXTURE: 72% (60-40, OCC-CN), 28% CCl 18°C

Solvents	*B. P.* *°C*	*Vapor Pressure Torr*	*Slope* $\frac{(m\mu)\ liter}{moles \times 10^{-4}}$
I. CHLORINATED METHANES			
a. Dichloromethane	40.1	351.2	2.78
b. Chloroform	61.3	171.6	12.07
c. Carbon Tetrachloride	76.8	89.9	2.63
II. AROMATICS			
a. Benzene	80.1	92.68	3.225
b. o-Xylene	144.4	4.341	54.54
c. m-Xylene	139.1	5.524	33.33
d. p-Xylene	138.4	5.695	26.31
III. HYDROCARBONS			
a. n-Hexane	69.0	109.3	0.0
b. Cyclohexane	81.4	66.53	2.745
c. n-Nonane	150.8	8.37	0.0
IV. ESTERS			
a. Ethyl Acetate	78.5	38.11	2.14

TABLE IV

LIQUID CRYSTAL MIXTURE: 80% (60-40, OCC-CN), 20% CCl, 18°C

Solvents	*B. P.* °C	*Vapor Pressure Torr*	*Slope* $\frac{(m\mu)\ liter}{moles \times 10^{-4}}$
I. CHLORINATED METHANES			
a. Chloroform	61.3	171.6	0.9564
b. Carbon Tetrachloride	76.8	89.9	0.1941
c. Dichloromethane	40.1	351.2	0.1592
II. AROMATICS			
a. Benzene	80.1	92.68	0.1339
III. HYDROCARBONS			
a. n-Hexane	69.0	109.3	—0.1578
b. n-Nonane	150.8	8.37	—0.1454
IV. ESTERS			
a. Ethyl Acetate	77.2	70.26	0.049

TABLE V

LIQUID CRYSTAL MIXTURE: 11.12% Cholesteryl Erucate
60.00% Cholesteryl Nonanoate
28.88% Cholesteryl Butyrate

Solvents	*B.P.* °C	*Vapor Pressure Torr*	*Slope* $\frac{(m\mu)\ liter}{moles}$ $x\ 10^{-4}$
I. CHLORINATED METHANES			
a. Chloroform	61.3	171.6	—15.94
II. AROMATICS			
a. Benzene	80.1	92.68	—1.785
III. HYDROCARBONS			
a. Cyclohexane	81.4	66.53	13.04

tion between dipole moment, configuration and sensitivity. In Figure 12 we compare the slope of chloroform to dichloromethane and carbon tetrachloride for the two mixtures.

Generally, the higher the vapor pressure the greater the response for a homologous series. In Figures 13 and 14 homologous series of straight chain ketones and straight chain alcohols are compared. We see also a relatively small sensitivity to alcohols compared to the lower boiling ketones. Generally, the straight chain isomers have a larger response than branch chains, as in the case of the 2-propanol and the 2-butanol.

A further comparison of the effect of substitution is made in Figure 15 which compares the response to straight chain esters of 24% cholesteryl chloride. In this case, again we see the effect of positional substitution. In that ethylacetate and methyl propionate are the same molecular weight, we have an increased sensitivity for methylpropionate.

The same type of substitution effect is shown with the ethylpropionate, propylacetate and methylbutyrate. This result shows that even isomeric compounds can be distinguished on the basis of the response of liquid crystals.

One of the interesting systems for discrimination is the cholesteryl butyrate, cholesteryl erucate, cholesteryl nonanoate system. In Figure 16 we see the response of typical cholesteryl chloride systems to benzene, cyclohexane, and chloroform. In all cases, we have a nearly linear response, although at low concentrations of cholesteryl chloride, we have a negative slope for the cyclohexane. In comparing this to the results with the cholesteryl butyrate, we see immediately a completely chained response. In the table we see slopes at low concentration. In the figure we see the slopes for benzene, cyclohexane and chloroform. Note that the direction of shift has been inverted and that the sensitivity to cyclohexane is very large. This system would be suitable for discrimination purposes, although the lack of linear slope would be somewhat of a handicap in determining concentration.

The reason for the strong non-linearity might be the presence of a liquid crystal phase of the smectic type at a lower temperature. The smectic type phase corresponds to an unwound structure which is generated by the bonding between the aliphatic chains. The cyclohexane, then, we suppose affects the aliphatic chains more strongly than the chloroform or the benzene. This is a very superficial explanation and will require much more study before a complete understanding is obtained.

The information provided in the tables clearly shows that qualitative information can be obtained by differential analysis of various liquid crystalline materials. In this case we find that our qualitative information requires a higher concentration than the corresponding quantitative information. However, by using an array of liquid crystals similar to the ones listed in our table, nearly complete analytical information could be obtained on any sample of pure vapor. At this time, no single explanation can describe completely the interactions of vapor with liquid crystals.

The experimental study of mixed vapor systems with liquid crystals has turned up a number of unusual effects. In Figure 18 the response of 24% cholesteryl chloride with mixtures of benzene and hexadecane are plotted and the slope determined. The tabular results, shown in Table VI, show no simple phenomena to be present. It would require much more complete study of the effects of mixed systems to be able to predict the result. This would indicate that our response of the liquid crystal depends somewhat upon solvation, that is, the power of a solvent to dissolve cholesteric esters. This is apparent from the increased sensitivity of the mixtures of benzene and cyclohexane since these combinations tend to be better solvents than cyclohexane alone. A total explanation of this effect would require considerably more measurements than were permitted by the time under this program.

PURITY OF MATERIALS

The materials prepared for gas sensing were generally in two categories. One is the basic substances used in compounding of materials (these are cholesteryl oleyl carbonate, cholesteryl nonanoate, cholesteryl chloride, cholesteryl butyrate, cholesteryl erucate), and the other is the materials prepared for additives, such as 3ß-carboxy-Δ5-cholestene, and the esters of this acid.

The purity of the materials in this program was seen to be very important. Very small inpurities in either the basic material or any additive contemplated clearly affected the outcome. The basic materials used for the cholesterol derivatives were chromatographically pure; particularly in the case of oleyl alcohol used in making the cholesteryl

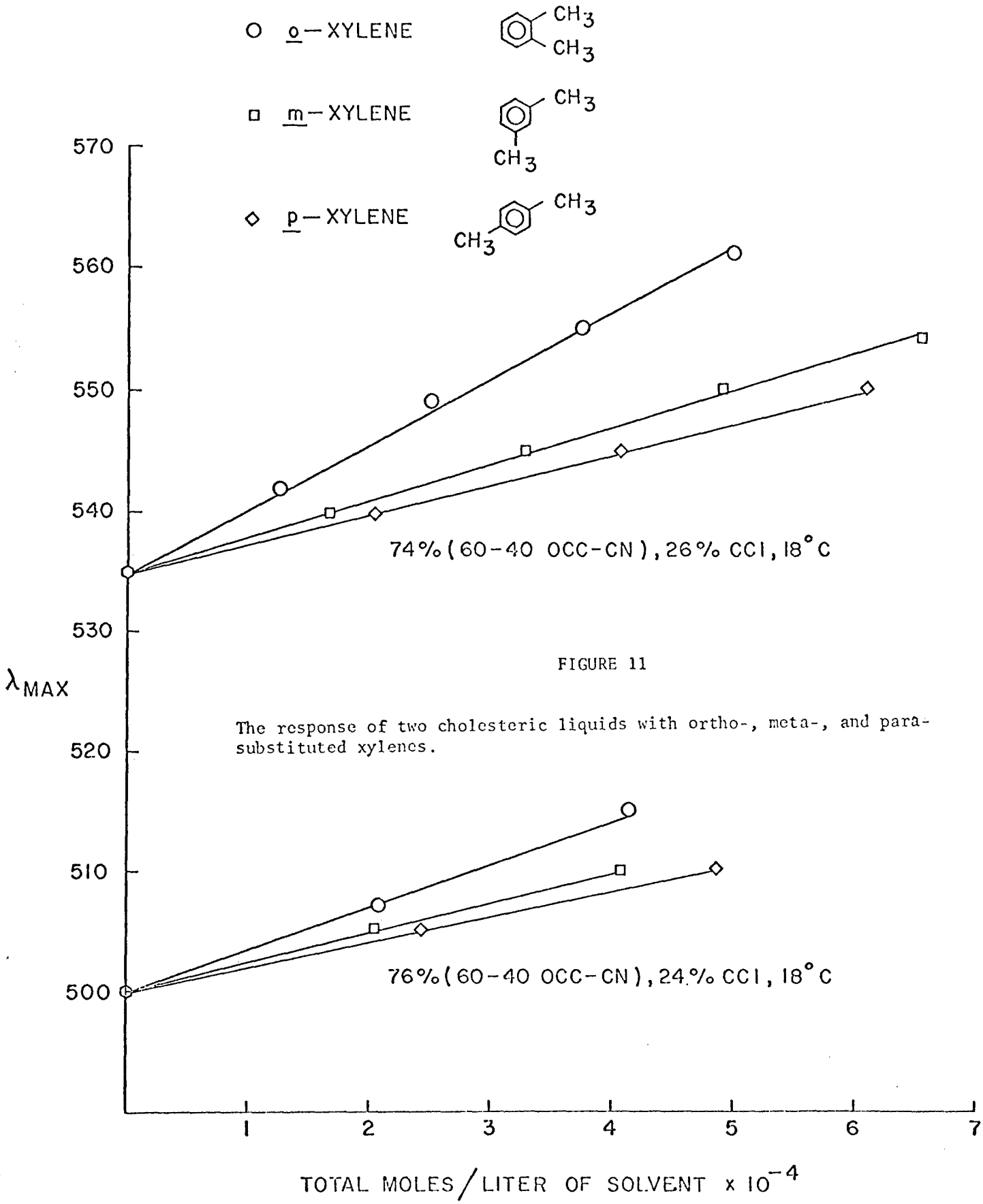


FIGURE 11

The response of two cholesteric liquids with ortho-, meta-, and para-substituted xylenes.

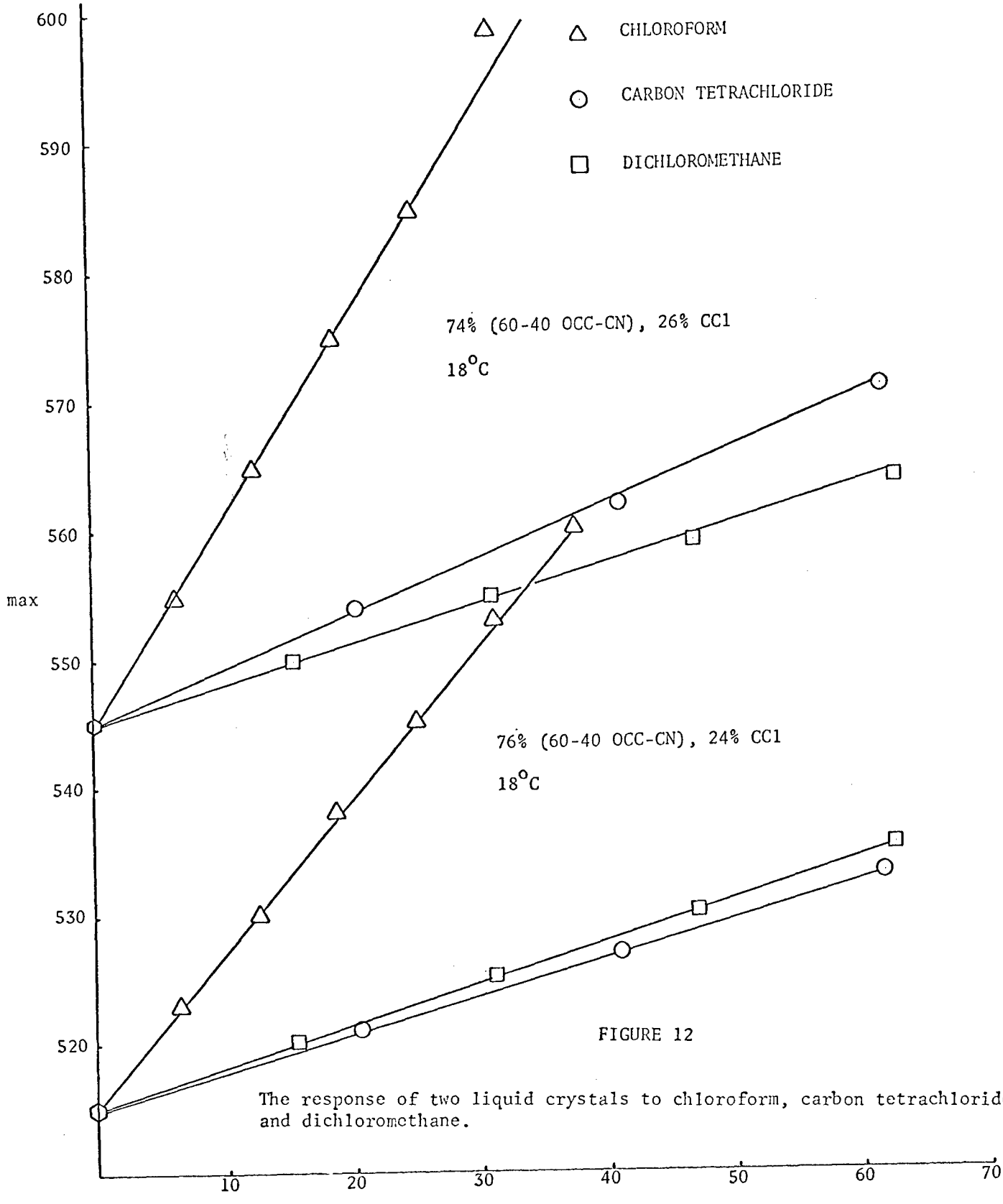


FIGURE 12

The response of two liquid crystals to chloroform, carbon tetrachloride and dichloromethane.

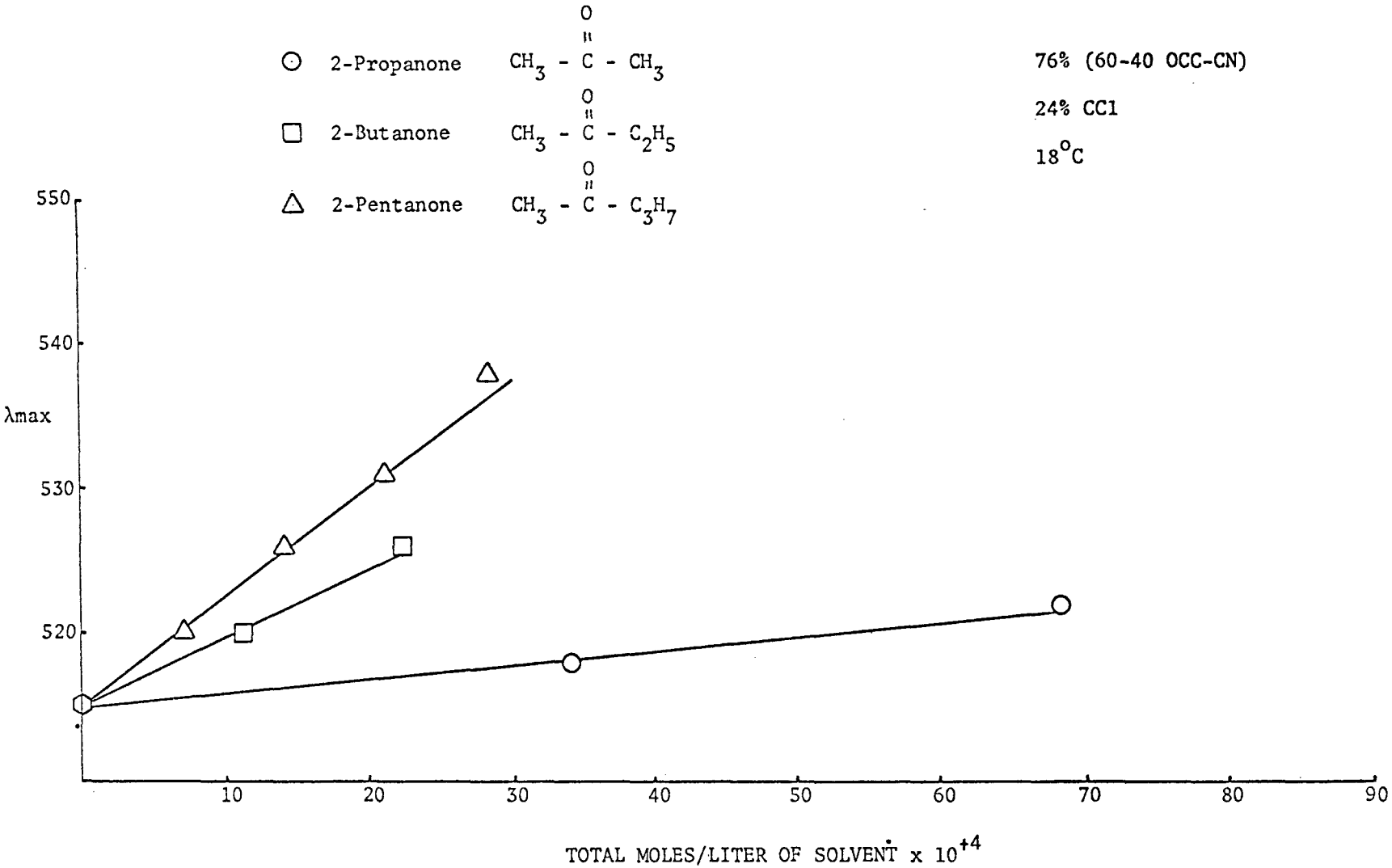


FIGURE 13

The response of straight chain ketones in 24% cholesteryl chloride, 60% cholesteryl oleyl carbonate - 40% cholesteryl nonanoate.

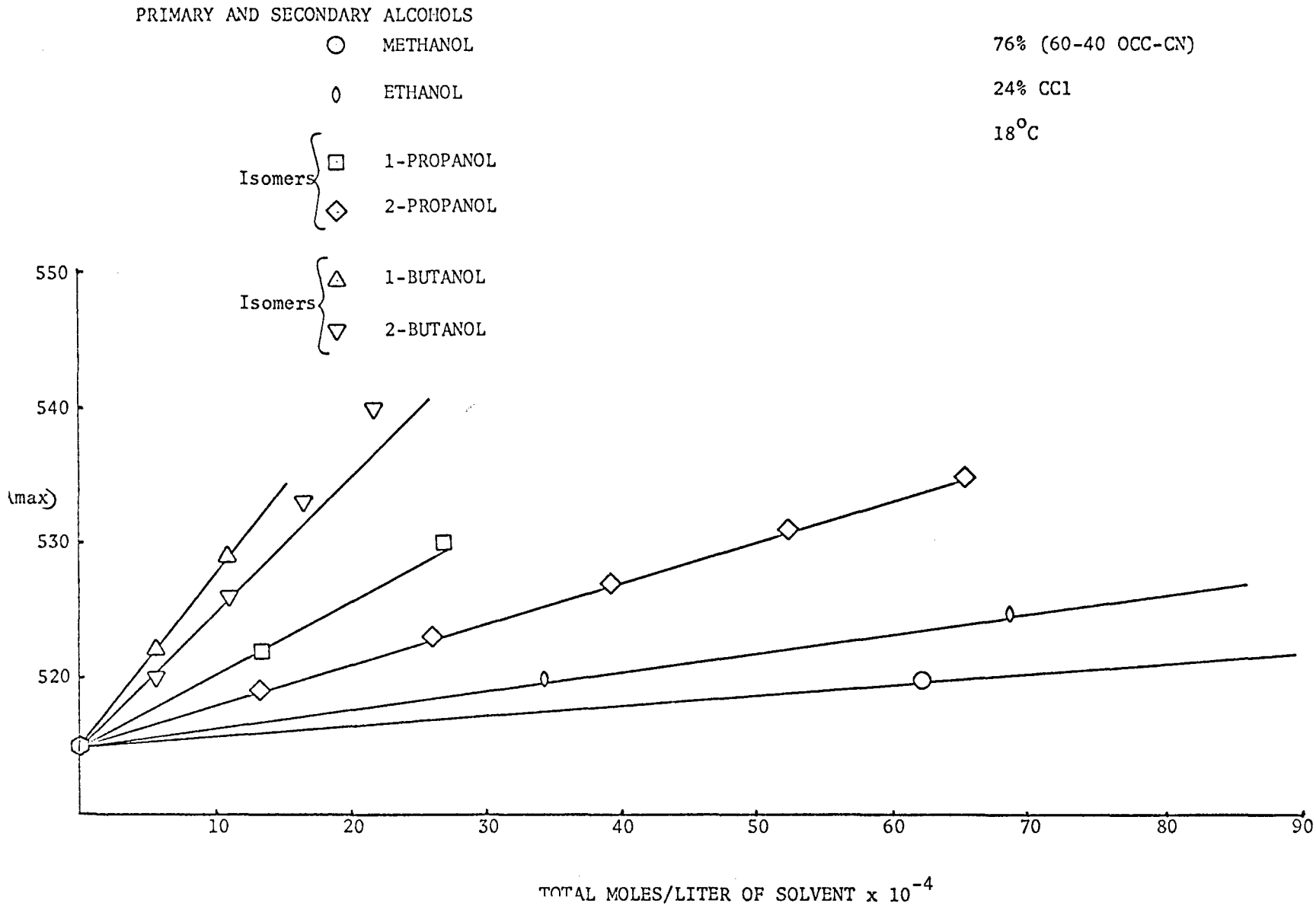


FIGURE 14

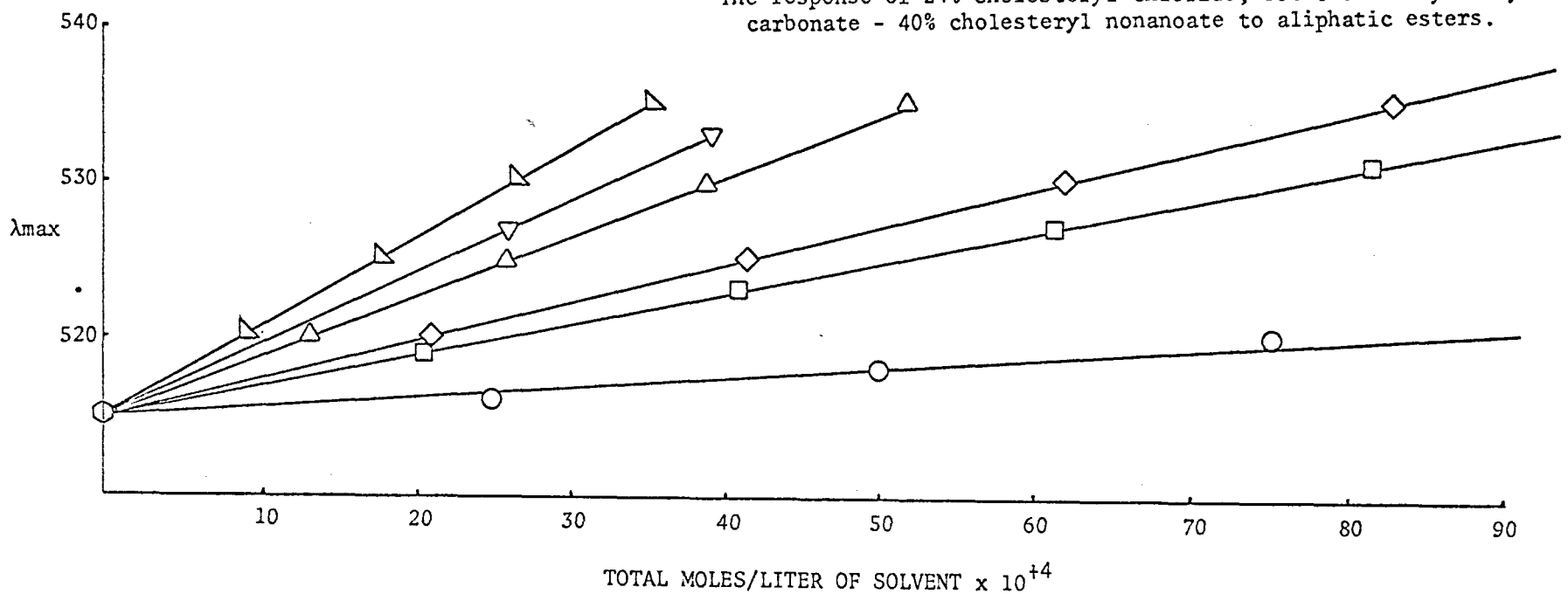
The response of alcohols in 24% cholesteryl chloride, 60% cholesteryl oleyl carbonate - 40% cholesteryl nonanoate.

STRAIGHT CHAIN ESTERS

Isomers	○ METHYL ETHANOATE	$CH_3 - \overset{O}{\overset{\|}{C}} - O - CH_3$	76% (60-40 OCC-CNO
	⊡ ETHYL ETHANOATE	$CH_3 - \overset{O}{\overset{\|}{C}} - O - C_2H_5$	24% CCl
	◇ METHYL PROPIONATE	$C_2H_5 - \overset{O}{\overset{\|}{C}} - O - CH_3$	18°C
Isomers	△ ETHYL PROPIONATE	$C_2H_5 - \overset{O}{\overset{\|}{C}} - O - C_2H_5$	
	▽ PROPYL ETHANOATE	$CH_3 - \overset{O}{\overset{\|}{C}} - O - C_3H_8$	
	◺ METHYL BUTYRATE	$C_3H_8 - \overset{O}{\overset{\|}{C}} - O - CH_3$	

FIGURE 15

The response of 24% cholesteryl chloride, 60% cholesteryl oleyl carbonate - 40% cholesteryl nonanoate to aliphatic esters.



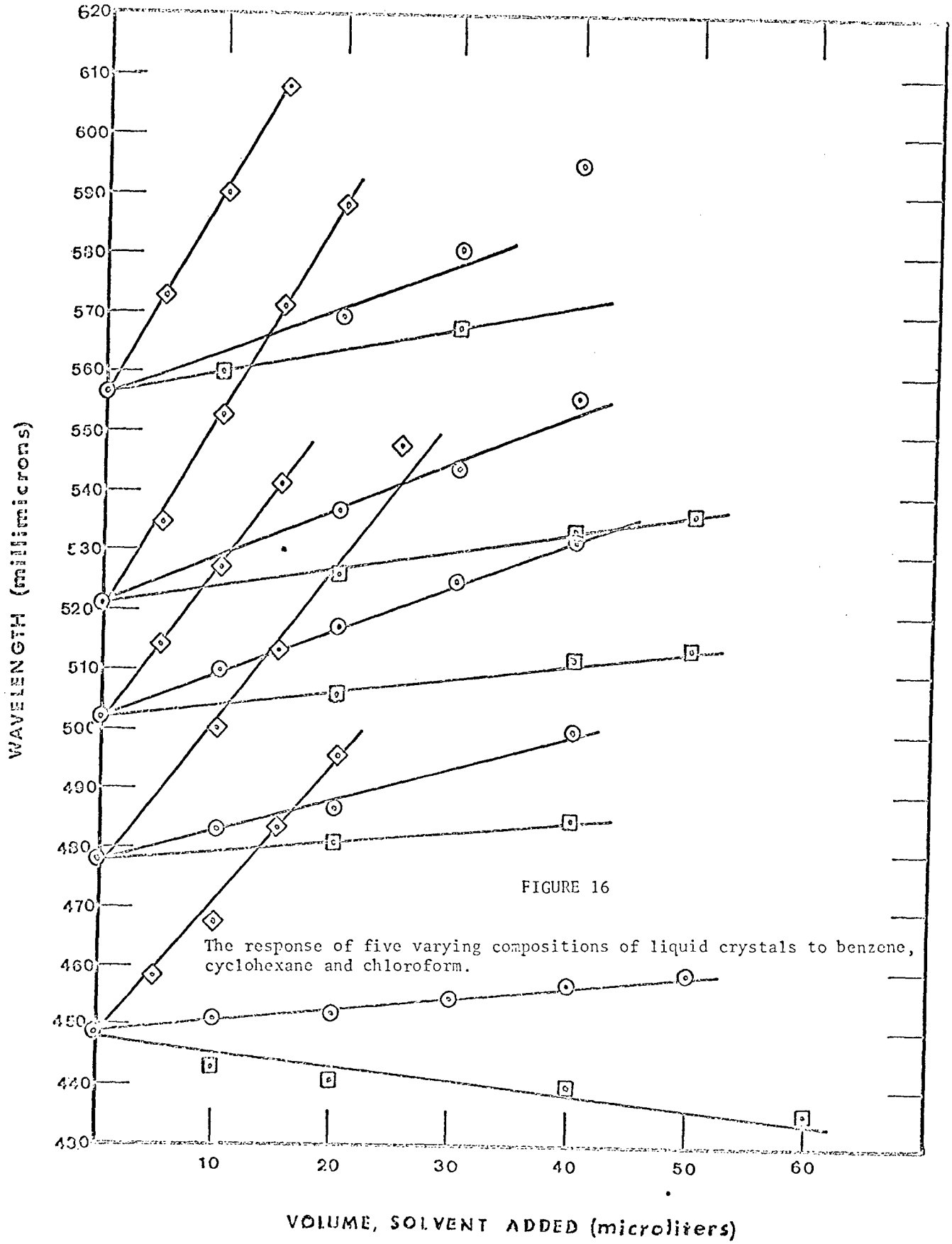


FIGURE 16

The response of five varying compositions of liquid crystals to benzene, cyclohexane and chloroform.

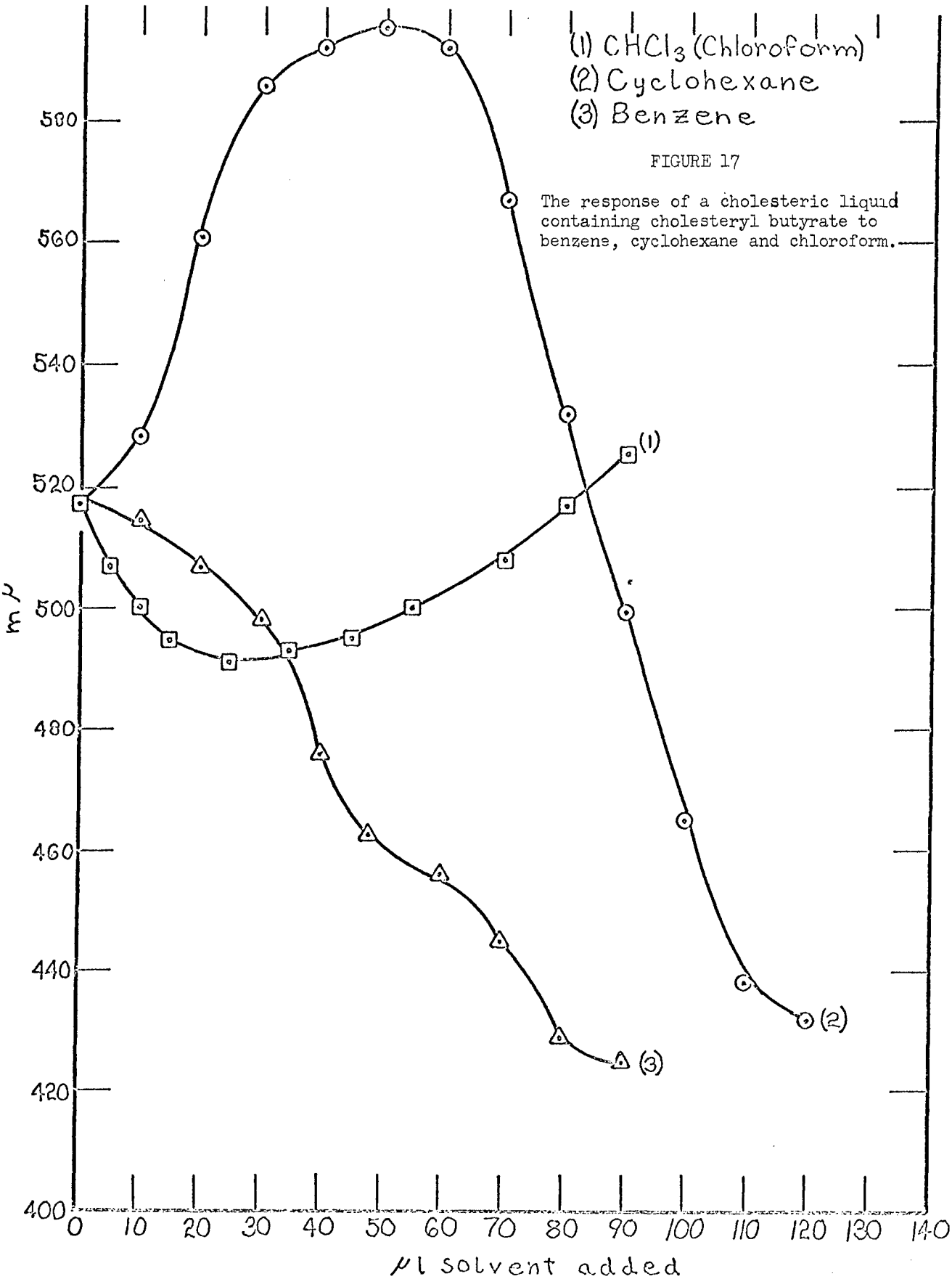


FIGURE 17

The response of a cholesteric liquid containing cholesteryl butyrate to benzene, cyclohexane and chloroform.

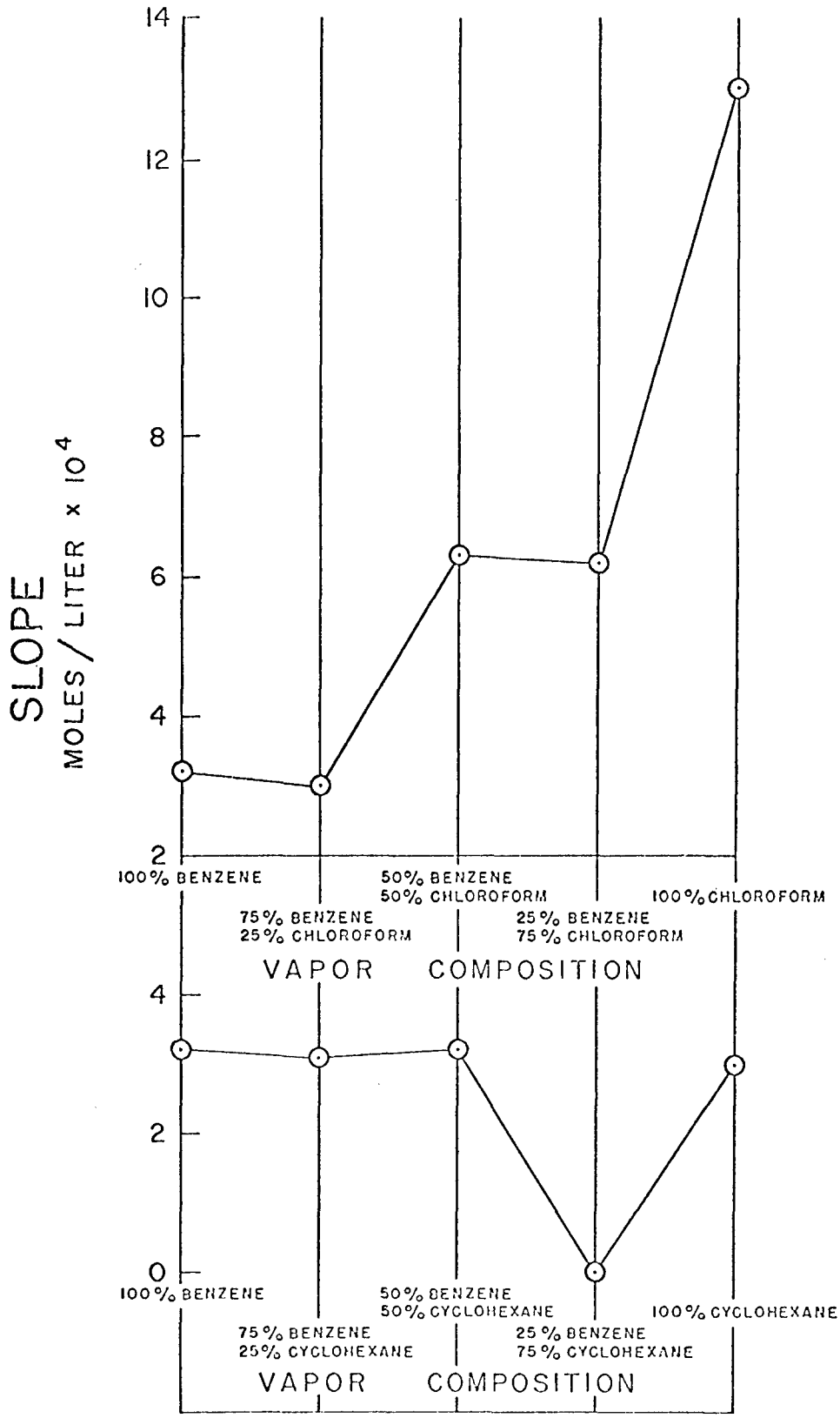


FIGURE 18 The effect of mixed solvents of 24% cholesteryl chloride in 60% cholesteryl oleyl carbonate - 40% cholesteryl nonanoate.

TABLE VI

LIQUID CRYSTAL MIXTURE 76% (60-40 OCC-CN), 24% CCl, 18°C	
Mixed Solvent	*Slope*
Benzene	3.2
Chloroform	13.02
Cyclohexane	2.95
50% Benzene, 50% Chloroform	6.3
25% Chloroform, 75% Benzene	3.03
25% Benzene, 75% Chloroform	6.19
50% Benzene, 50% Cyclohexane	3.2
25% Cyclohexane, 75% Benzene	3.06
25% Benzene, 75% Cyclohexane	0.0

oleyl carbonate, we used 99.9% material which had been vapor-phase chromatographed.

The criterion for purity was differential thermal analyzer (DTA) and chromatograph. As a merk of purity, the compositions we list could be repeated with identical results in terms of gas-sensing between synthetic batches. Therefore, we feel that with good reproducibility, the material was sufficiently pure. The materials which we prepared for additives were not sufficiently tested in gas-sensing. This would have been a continuing part of the program; however, the preparative work led to the publishing of several interesting results (refs. 4 and 5).

The compounds were prepared in the following manner:

Cholesteryl Butyrate: 386 grams (1 mole) of cholesterol is dissolved in 220 ml dry benzene with 79.1 gms (1 mole) of pyridine added. To this mixture 106.5 gms (1 mole) of butyryl chloride is added dropwise with constant stirring to the cool solution. After refluxing for 3 hours, the reactant mixture is cooled, the pyridine hydrochloride filtered off and the cholesteryl butyrate is precipitated with methanol, filtered and recrystallized from acetone. The crude melts at 96.5°C, clears 108.5°C; recrystallized melts 99.0°C, clears 108.5°C. Crude yield is nearly 100%.

Cholesteryl Chloride: 386 gms (1 mole) of cholesterol is dissolved in 2200 ml of dry benzene to which 118.9 gms (1 mole) of thionyl chloride is added dropwise to the vigorously stirred cholesterol solution. After addition of the thionyl chloride, the mixture is heated to reflux for 2 hours, after which the reactant mixture is reduced to half-volume. The cholesteryl chloride is precipitated with methanol, filtered and recrystallized from acetone. The crude cholesteryl chloride melts 93.0°C, clears 14.5°C; recrystallized melts 94.0°C and clears 95.0°C. The crude yield is about 90%.

Cholesteryl Erucate: To 338.6 gms (1 mole) of erucic acid in 700 ml of dry benzene, 118.5 gms (1 mole) of thionyl chloride is added dropwise. After addition of all of the thionyl chloride, the reaction mixture is brought to reflux for 1 hour, then cooled and 386.5 gms (1 mole) of cholesterol, together with 79.1 gms (1 mole) of pyridine in 2200 ml of dry benzene, is added. This mixture is brought to reflux for 3 hours, then cooled and the pyridine hydrochloride formed is filtered off. The crude cholesteryl erucate is precipitated from the mother liquor as an oil with methanol, washed several times in absolute ethanol and then placed under the vacuum of an aspirator over a steam bath to remove any excess ethanol. The purified yield is 50-60%.

Cholesteryl Nonanoate: To 386.5 gms (1 mole) of cholesterol with 79.1 gms (1 mole) of pyridine in 500 ml of dry benzene, 176.7 gms (1 mole) of nonanoyl chloride is added; the pyridine hydrochloride is then filtered hot, the mixture cooled to about 45°C and the crude cholesteryl nonanoate precipitated with methanol. It is recrystallized from acetone. The crude material melts at 73°C and clears at 87.5°C; recrystallized melts 76°C and clears 88.5°C. The recrystallized yield is about 85%.

Cholesteryl Oleyl Carbonate: 99.0 gms (1 mole) of phosgene is bubbled into 1000 ml of dry benzene to which is added with rapid stirring 386 gms (1 mole) of cholesterol and 79.1 gms (1 mole) of pyridine in 2600 ml dry benzene. After 30 minutes of stirring, the pyridine hydrochloride formed is filtered off and 268.0 gms (1 mole) of oleyl alcohol is added together with 79.1 gms (1 mole) of pyridine. This mixture is allowed to stir 3 hours after which the pyridine hydrochloride formed is removed by filtration and the crude cholesteryl oleyl carbonate is precipitated with methanol as an oil. It is washed several times with absolute ethanol; after which, any excess alcohol is removed over a steam bath under the vacuum of water aspirator. The purified yield is 50-60%.

SECTION IV

SENSITIVITY

The sensitivity of liquid crystals to vapor was treated both on a theoretical basis and an experimental basis. Since we observe in the cholesteric liquid a color change which is based on a structural reorganization, the effect will depend upon the molar concentration per unit area. That is, if we have a volume of cholesteric liquid, the uncertainty in concentration of a given volume in the grand conanical ensemble will be $\Delta n = \sqrt{\bar{n}}$, where $\bar{n}$ is the average number of molecules per unit volume. It is now up to us to determine the size of the volume which is important in determining our mechanical structure.

The mechanical structure has a response time of 1/10 second. That is to say that a change in structure requires 1/10th second to arrive at a new equilibrium orientation after an applied stimulus, such as electric field, temperature or change in concentration. If we, therefore, consider a gas molecule which is diffusing in the material, we can define a characteristic length through which the molecule would diffuse within 1/10 second, and no response of the liquid crystal would be able to localize our molecules to a smaller dimension. That is, the molecular reorganization must be averaged over at least one diffusion length.

To obtain a value for the diffusivity (δ), we placed the 24% cholesteryl chloride, 45.6% cholesteryl nonanoate, 30.4% cholesteryl oleyl carbonate between two glass slides such that the edge was exposed. We placed this in a sealed chamber at 24°C in equilibrium with the chloroform vapor. By observing the rate of diffusion from the edge into the center of the slide, we were able to get a measurement of the diffusivity of chloroform. At 24°C this was 2×10^{-7} cm^2/sec. Our characteristic length (L) is now

$$L = \sqrt{\delta \cdot t},$$

where t = time. For the 24% mixture of cholesteryl chloride, this is 1.4×10^{-4} cm or 1.4μ. That is to say, our basic volume for detection of 1 molecule of vapor is $(1.4\mu)^3$. Since we need an optimum detector volume of 6.25×10^{-7}cc (.01 x .01 inch square film, 10μ thick), our minimum detectable number of molecules would be $\sqrt{2.2 \times 10^5}$ with a signal to noise ratio of 1. The maximum sensitivity is, therefore, 3×10^{-19}gm for chloroform within the liquid crystal. This, however, implies perfect detection of the shift in wavelength. Our system is limited by our ability to measure the shift in wavelength due to impurities and not by the statistical noise of the molecules themselves.

The limit of our system by the electronic system and thermal fluctuation noise in the liquid crystals can be expressed as follows: The energy required to change the pitch is:

$$E = \frac{kV}{2} \times \left(\frac{1}{P_1}\right)^2 - \left(\frac{1}{P_2}\right)^2,$$

where k is a force constant equal to 10^{-6} dynes, V is the volume, and P is the pitch where the subscripts represent the initial and final states.

If we set the energy equal to kT, or 4.4×10^{-14} erg, and the volume equal to the volume of our detector, we find the limiting value of the change in pitch is 10^{-6} μm for a wavelength of 550 μm. Since we express the results of our data in terms of slope in μliters/mole, we could express the limiting sensitivity (S), where a is the slope, as

$$S = \frac{10^{-6}\,m}{a} \cdot$$

This limiting sensitivity applied to our measurements gives a limiting concentration expressed in grams/meter^3:

$$C_L = (MW)\, S \times 10^3,$$

where MW is the molecular weight, or 1 microgram/cubic meter for the example stated above. Our results verify that this measurement can generally be used as limiting sensitivity.

To verify this, we have attempted to measure the smallest concentration we can introduce in the controlled atmosphere chamber by injecting fractions of a microliter and

measuring the change in intensity. The results are plotted in Figure 19. We note that in this figure, the noise is approximately .01 of a signal. The sample injected was 0.1 microliter or 10 micrograms/liter. Our minimum detectable level, then, would have been .01 of this, or 0.1 micrograms/liter or 100 micrograms/cubic meter.

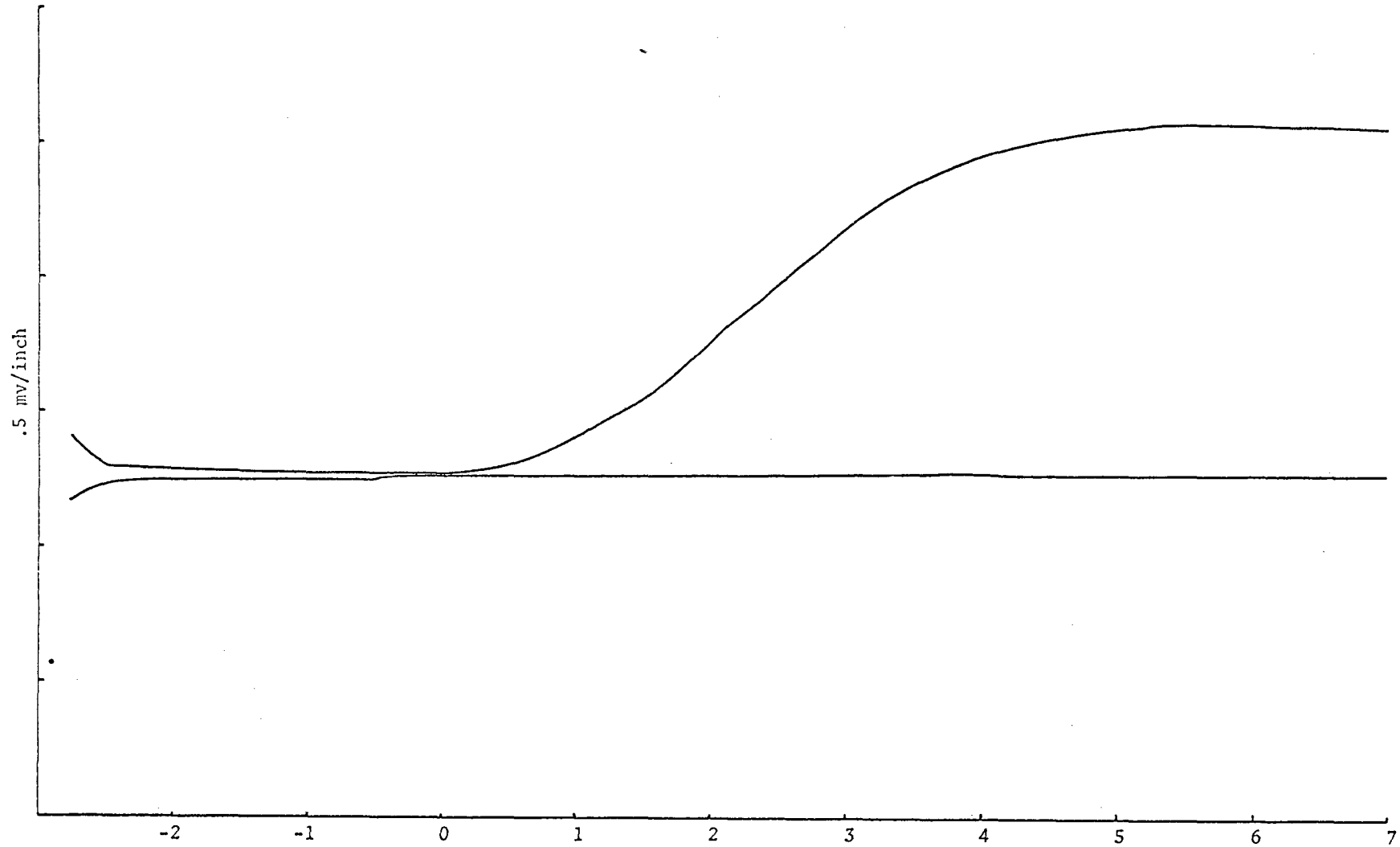


FIGURE 19

Maximum sensitivity shown by a mixture of 5% cholesteryl chloride in 60% cholesteryl oleyl carbonate - 40% cholesteryl nonanoate.

APPENDIX I

PREPARATION OF 3ß-CARBOXY DERIVATIVES OF CHOLESTENE

INTRODUCTION

The principal aim of this research was the preparation of the 3-carboxyl derivative of cholesterol and its derivatives (esters of 3ß-carboxy-5-cholestene). This objective has been achieved, although not without the difficulties which will be described below.

Most of the compounds prepared by us displayed liquid-crystalline properties, as determined by polarizing-microscopy.

DISCUSSION AND EXPERIMENTAL DETAILS

(a) 3ß-carboxy-5-cholestene

The preparation of this acid is difficult, due to the inactivity of both the 3ß-chloro and the 3ß-bromo derivative used as a precursor in the Grignard reaction. The ultimate procedure, employed after many unsuccessful attempts, is a combination of procedures described in references 6 through 10.

The principal difficulty in the preparation, next to the inactivity of the halide towards magnesium was the formation of bicholesteryl as the most significant side-product, often difficult to separate from the desired product. Contrary to most organic acids, the desired acid was completely insoluble in aqueous NaOH and KOH solutions.

The best procedure is as follows: A three-neck flask, equipped with a pressure-compensated dropping funnel, Hirschberg stirrer and condenser, fitted with a $CaCl_2$ drying tube, is scrupulously dried with a free flame. A nitrogen inlet is attached to the dropping funnel and nitrogen gas is allowed to enter when the apparatus is cooled, to prevent the reentry of atmospheric moisture. 200 ml of anhydrous ether (from a freshly opened can) is introduced into the vessel, as well as 5 equivalents of magnesium turnings, which were crushed in a mortar just prior to addition. (In our runs, using 0.1 mole of halide, 12 g. of Mg was sufficient.) Next 0.1 mole of ethylbromide is added fairly rapidly, allowing a brisk reaction to take place. The desired amount of halide (0.1 mole) is then introduced slowly over a period of 3 hours in 200 ml of ether, while the mixture is stirred under reflux.

An alternate method, which we have found to be at least as successful if not superior, is to introduce 40 ml of CH_3I, instead of ethylbromide, and after 10 hours following addition of the halide of cholesterol, another 10 ml is introduced. In this fashion one is dealing with a replacement rather than a direct Grignard reaction.

The resulting mixture is allowed to reflux (with stirring) for 40 hours if bromide is used, and for 72 hours if chloride is used. After this time the solution is cooled somewhat, and freshly crushed dry ice is introduced through a powder funnel. After an initial exothermic reaction the solution cools down to lower temperatures. A large excess of CO_2 is added while stirring is continued as well as is possible in the thickening mixture. The solution is allowed to stand until room temperature is reached again, at which time ice-cold 2N (or 10%) H_2SO_4 is added.

Rather than wait for all excess magnesium to react, it is convenient at this time to remove the aqueous phase, after the addition of sufficient ether to dissolve most organic matter. There will be solid magnesium as well as finely powdered bicholesteryl left in the ether layer and interface, which does not significantly hinder layer-separation in the separatory funnel. The aqueous layers are extracted twice with ether, and are then discarded. The combined ether layers are filtered with gravity through a fluted funnel, dried with Na_2SO_4 and evaporated. The solid left on the fluted paper is largely bicholesteryl (m.p. 267-269°C) and is discarded. The residue is taken up in benzene and decolorized if necessary with some charcoal. Cooling in the refrigerator produces white crystals, m.p. varying from 217 to 226°C, depending on the run. (Similar variation is noted in the references cited.) The best yield obtained in any one run has been 30%, based on 3β-chloro-5-cholestene.

(b) 3ß-bromo-5-cholestene

This bromide was prepared without difficulty following the procedure described by G. Roberts, C. W. Shoppee and R. J. Stephenson, J. Chem. Soc., 2705 (1954).

One uses cholesterol dissolved in $CHCl_3$ to which N,N-dimethylaniline has been added. $SOBr_2$ is added to 20° (ice cooling) and after ethanol is added to the mixture, the product drops out. Recrystallized from acetone, it melts at 97-98°C.

(c) 3ß-chloro-5-cholestene

This compound had been prepared prior to the start of our work in the routine reaction of cholesterol, $SOCl_2$ and DMF.

(d) Preparation of esters of 3ß-carboxy-5-cholestene

The following generalized procedure was employed throughout: To 3g. of cholesterol-3ß-carboxylic acid (3ß-carboxy-5-cholestene) dissolved in 20 ml of dry benzene was added 10 ml of $SOCl_2$. The resulting mixture was refluxed for 2 hours, after which the entire mixture was evaporated under reduced pressure in a warm water bath. The resulting crude acid chloride was taken up in 20 ml of benzene and the desired alcohol is added in excess (5 equivalents), together with 10 ml of DMF. This mixture is once again stirred and refluxed for two hours, after which it is allowed to cool and is poured into ice-cold water (in a separatory funnel). The water layer is separated, if necessary, after further benzene is added to the mixture, and the organic phase is dried over Na_2SO_4. The solvent is removed under reduced pressure and the residue, consisting of the desired product and the excess alcohol, is taken up in ethyl acetate (hot) and allowed to cool. If no solid does separate, the mixture is heated again and ethanol is added to the filtrate to recover a second crop. Recrystallization is performed from ethyl acetate, with charcoal decolorization if necessary.

For the preparation of analytically pure samples, an evaporative distillation was carried out on the solid samples, using a Kugelrohr, at temperatures up to 280°C at 0.01 mm Hg. The resulting solids were crystallized from ethyl acetate one further time. The esters described below were prepared in this fashion.

I. Phenyl ester of 3ß-carboxy-5-cholestene:

Prepared using phenol as alcohol. M.p. 106-107°C. White needles; refractive in polarizing microscope; liquid crystalline properties.

% Composition Calcd. for $C_{34}H_{50}O_2$: C, 83.21; H, 10.26
Found: C, 82.95; H, 9.94

II. Benzyl ester of 3ß-carboxy-5-cholestene:

Prepared using benzyl alcohol. M.p. 87-88°C. White needles; doubtful liquid crystalline properties.

% Composition Calcd. for $C_{34}H_{50}O_2$: C, 83.27; H, 10.38
Found: C, 83.08; H, 10.16

III. Phenylethyl ester of 3ß-carboxy-5-cholestene:

Prepared from phenylethyl alcohol. M.p. 121-122°C.

% Composition Calcd. for $C_{36}H_{54}O_2$: C, 83.34; H, 10.49
Found: C. 83.17; H, 10.54

IV. Butyl ester of 3ß-carboxy-5-cholestene:

Prepared from butyl alcohol (normal). M.p. 63-64°C.

% Composition Calcd. for $C_{32}H_{54}O_2$: C, 81.64; H, 11.56
Found: C, 81.65; H, 11.70

V. trans-2-decalyl ester of 3ß-carboxy-5-cholestene:

Prepared from trans-2-decalol (courtesy of Dr. Fort). M.p. 128-130°C.

% Composition Calcd. for $C_{38}H_{62}O_2$: C, 82.84; H, 11.34
Found: C, 82.97; H, 11.37

VI. p-Iodophenyl ester of 3ß-carboxy-5-cholestene:

Prepared from p-iodophenol. Not analyzed due to lack of purity.

NOTE: Some other esters have been prepared and reported by L. Worrell and J. E. Sinsheimer, J. Am. Pharm. Assoc., *43*, 562 (1954).

Unsuccessful attempts made:

I. 5-cholestenyl Lithium

An attempt was made to prepare the lithium derivative, using the chloride as starting material, by refluxing it with clean lithium ribbon in ether for five days. Lithium was recovered unchanged and the procedure was abandoned, since it looked unpromising and we could make the Grignard more successfully.

II. ß-Norsteroids

It was thought that ß-Norsteroids might have interesting liquid crystalline properties, and we set out to prepare the ß-Nor- derivative of cholesterol. Our attempted procedure involved the oxidation of the B-ring, with CrO_3, followed by cyclization of the resulting keto acid and pyrolysis of the lactone thus obtained. The procedure to be followed was that of F. Sorm and H. Dykova, Collect. Czechoslov. Commun. *13*, 407 (1948), starting with cholesteryl acetate. The latter was prepared in a conventional manner from acetic anhydride and cholesterol. Upon attempting the chromium trioxide oxidation, however, we ran into unsurmountable separation and isolation problems, mainly because the desired product is but a minor product of the reaction. A second attempt, using $KMnO_4$ as oxidant was equally unsuccessful. We abolished the attempted synthesis.

APPENDIX II

LIQUID CRYSTAL RESPONSE CURVES

We have collected the response of various liquid crystals to vapor and collated their curves in the following section. They are arranged in the order that they are found in Tables I through V. This represents experimental data and can be used much the same way as an infrared spectra of a vapor might be used.

FIGURE 20

Solvent: DICHLOROMETHANE

76% (60-40 OCC-CN), 24% CCl

18°C

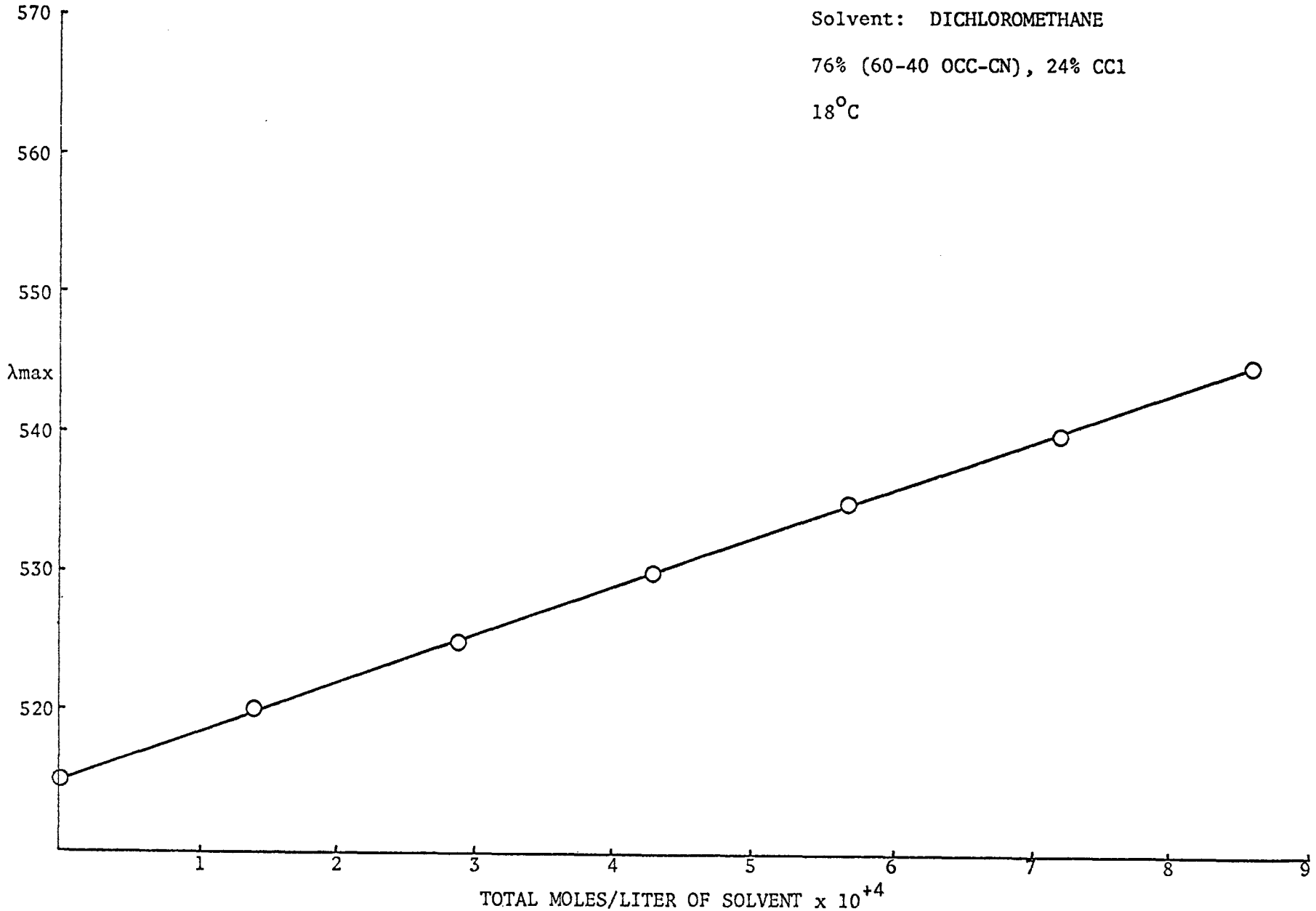


FIGURE 21

Solvent: CHLOROFORM

76% (60-40 OCC-CN), 24% CCl

18°C

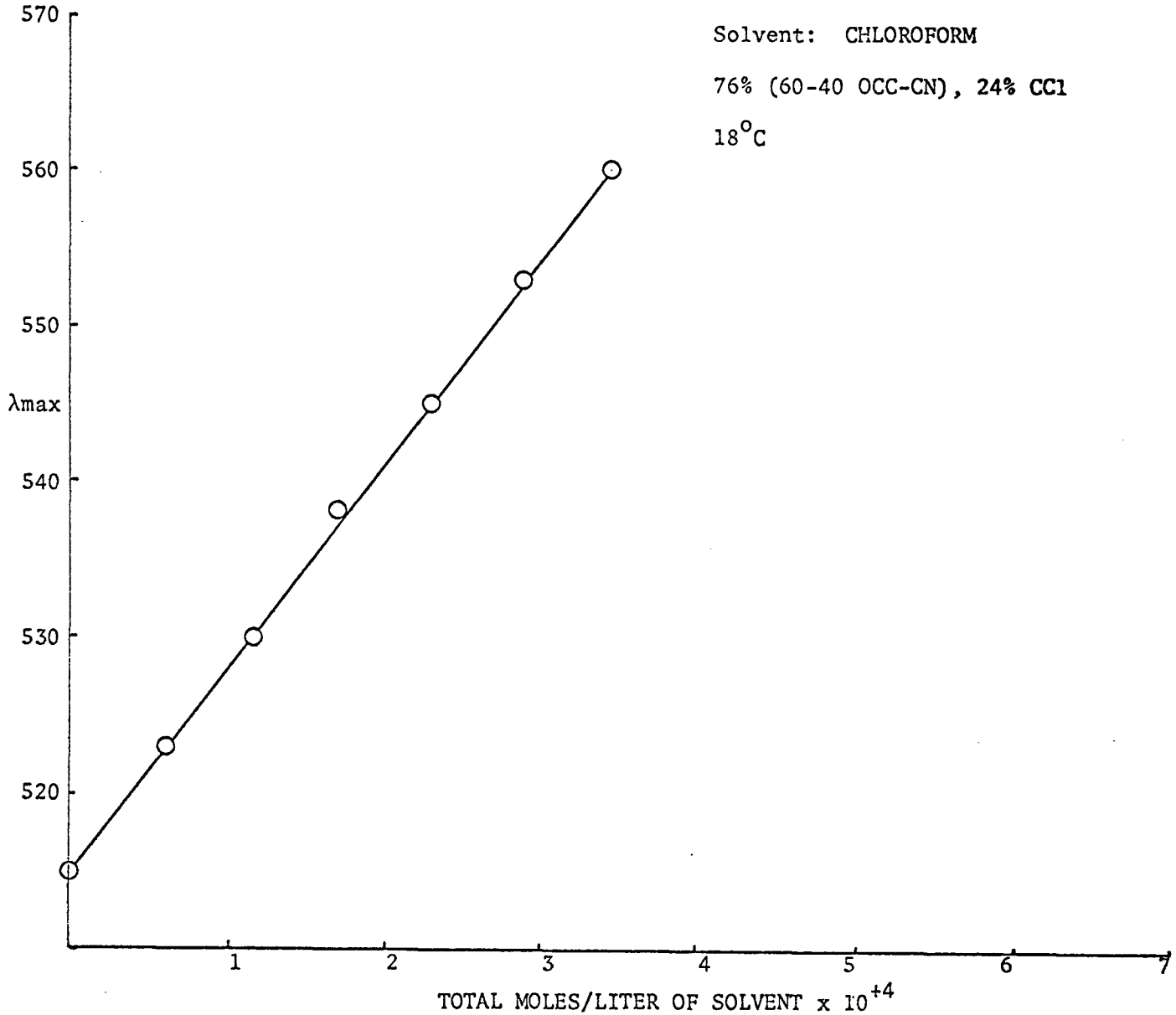


FIGURE 22

Solvent: CARBON TETRACHLORIDE

76% (60-50 OCC-CN), 24% CCl

18°C

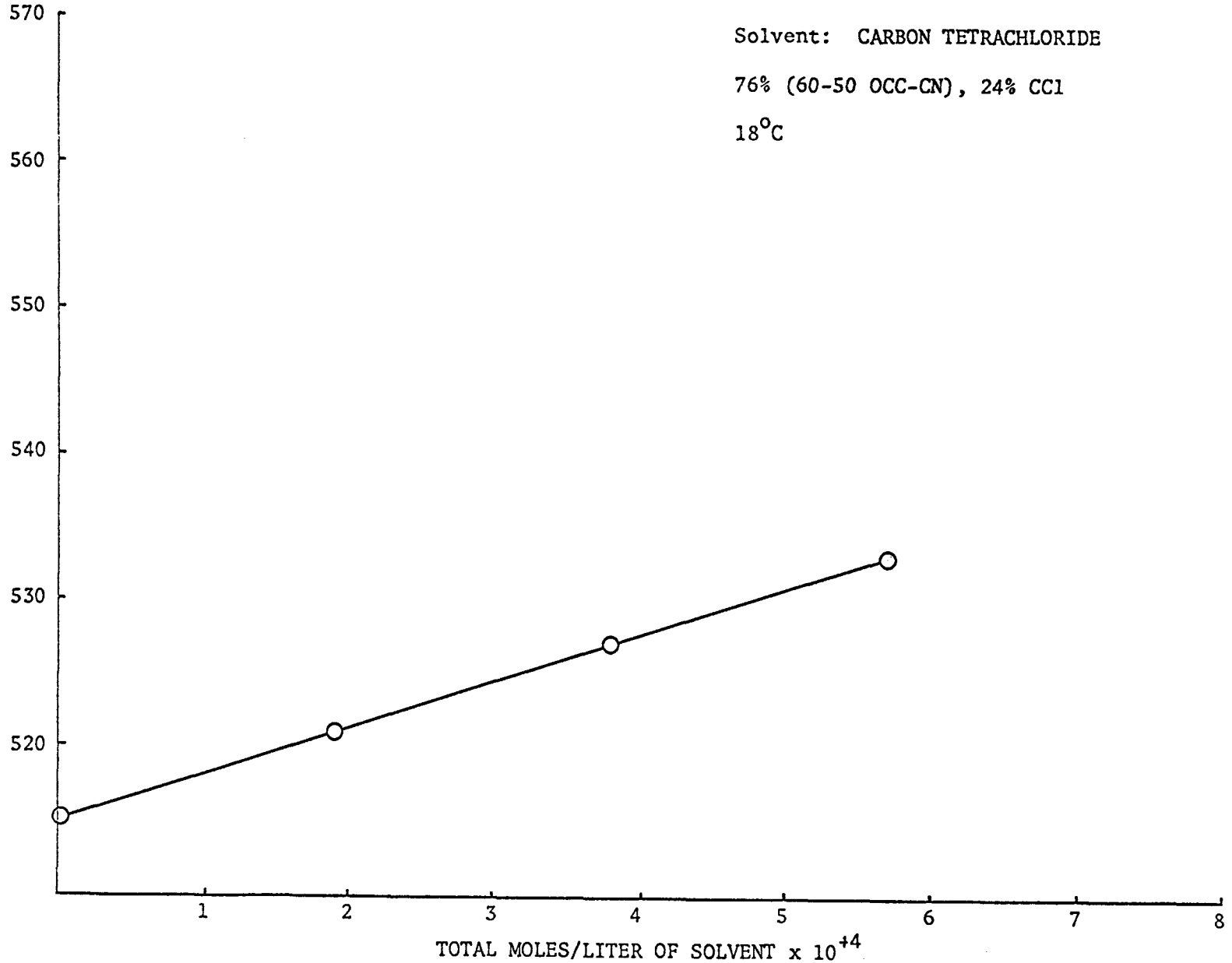


FIGURE 23

Solvent: BENZENE

76% (60-40 OCC-CN), 24% CCl

18°C

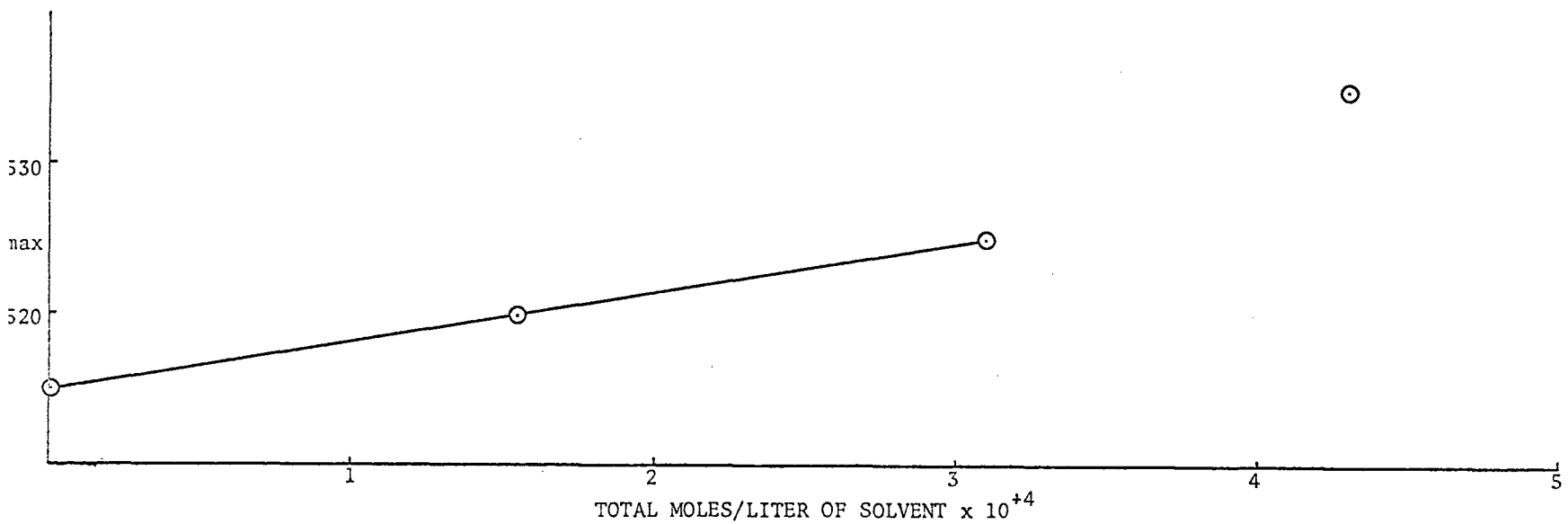


FIGURE 24

Solvent: TOLUENE

76% (60-40 OCC-CN), 24% CCl

18°C

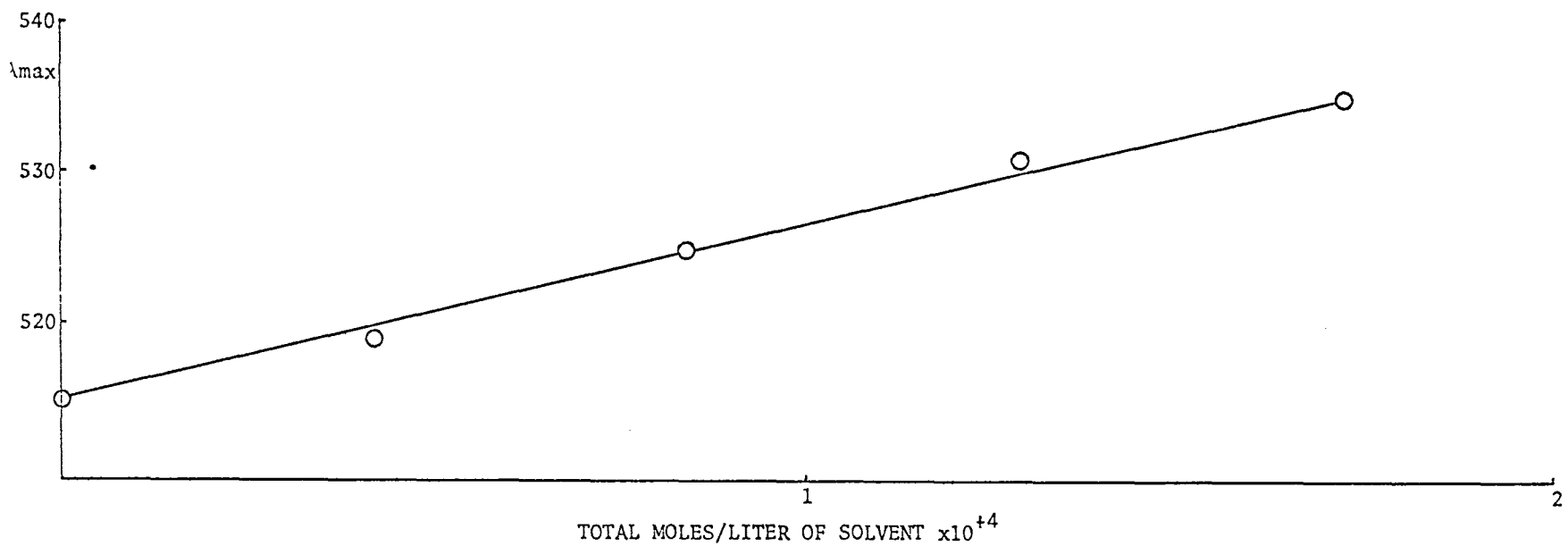


FIGURE 25

Solvent: o-XYLENE

76% (60-40 OCC-CN), 24% CCl

18°C

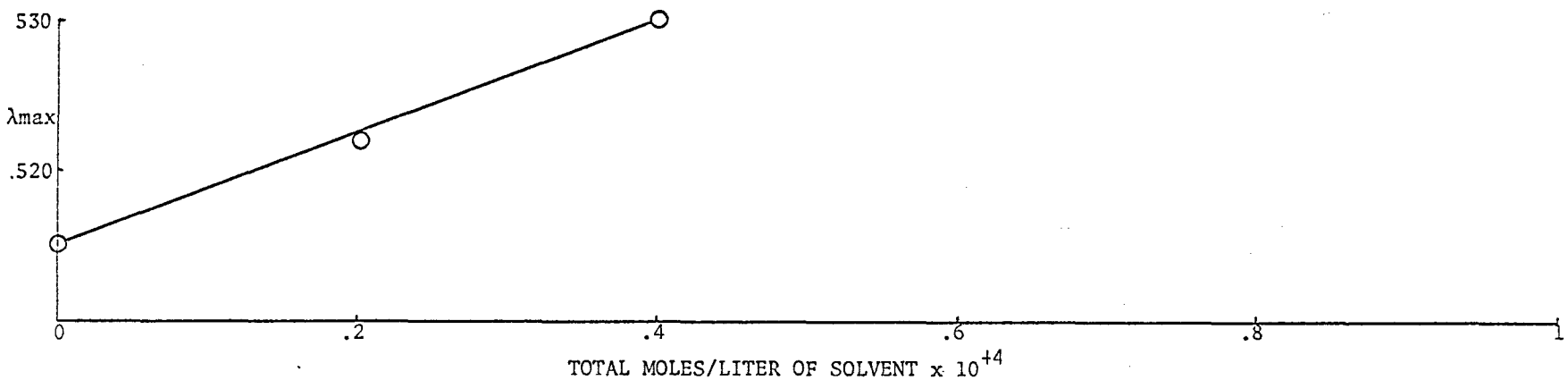


FIGURE 26

Solvent: m-XYLENE

76% (60-40 OCC-CN), 24% CCl

18°C

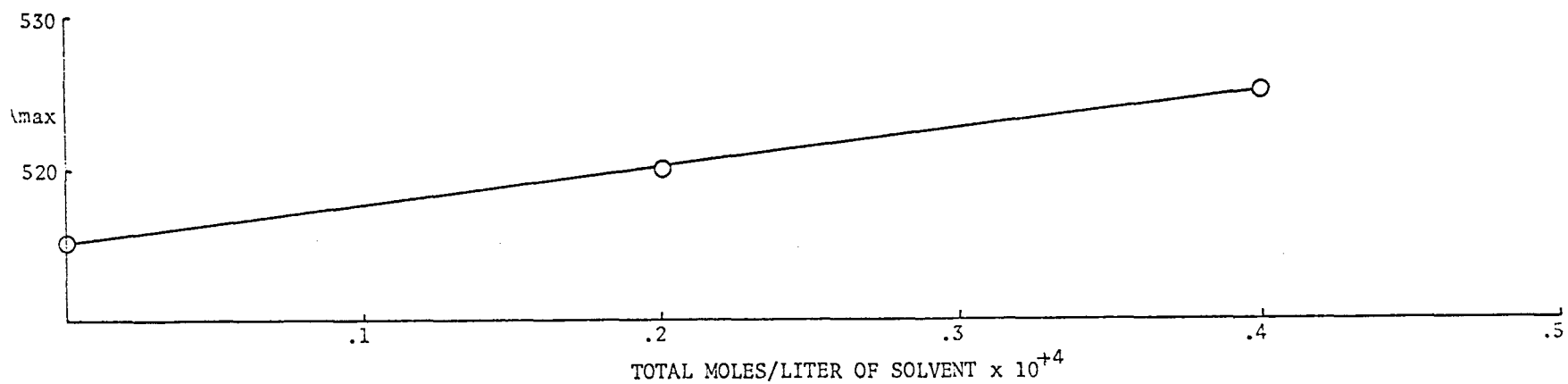


FIGURE 27

Solvent: p-XYLENE

76% (60-40 OCC-CN), 24% CCl

18°C

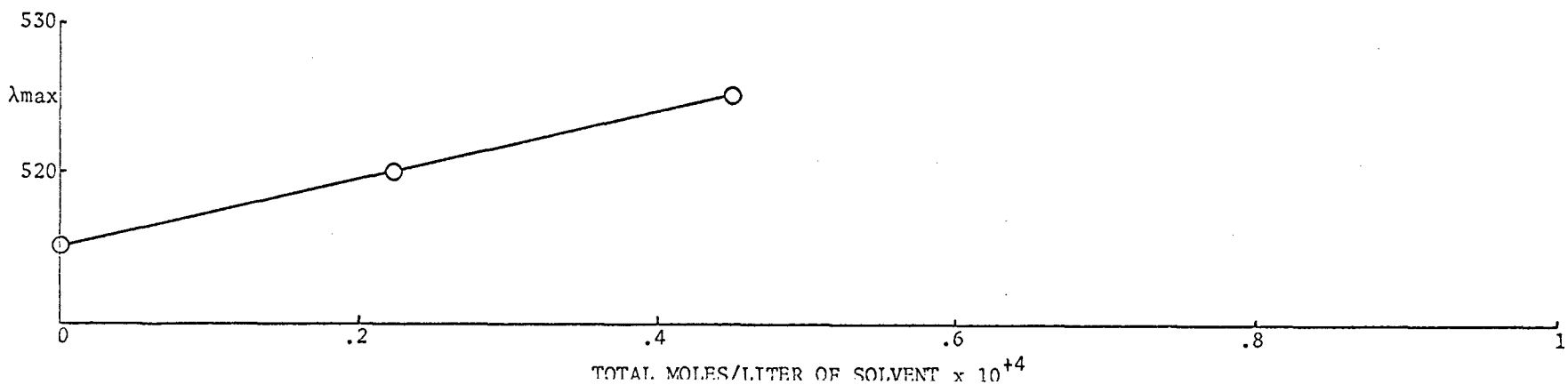


FIGURE 28

Solvent: FLUOROBENZENE

76% (60-40 OCC-CN), 24% CCl

18°C

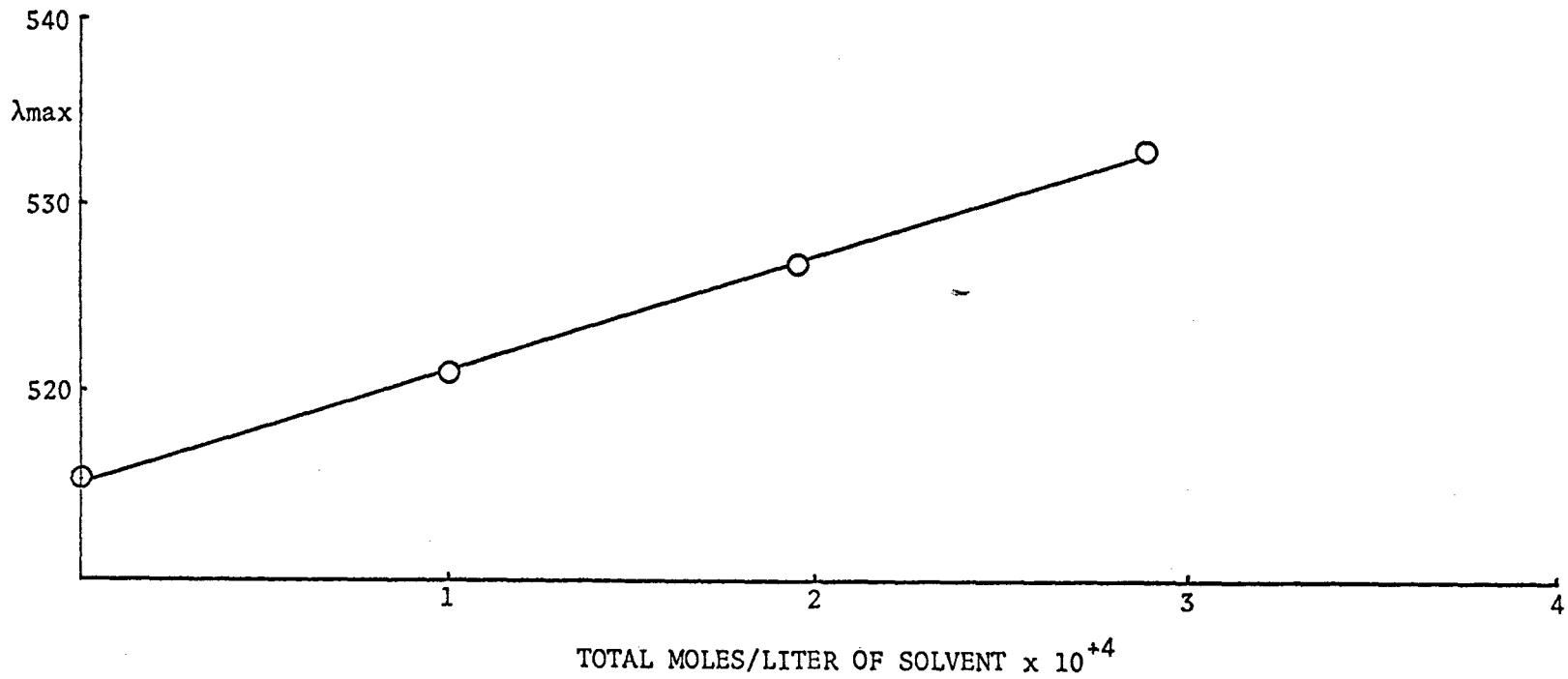


FIGURE 29

Solvent: CHLOROBENZENE

76% (60-40 OCC-CN), 24% CCl

18°C

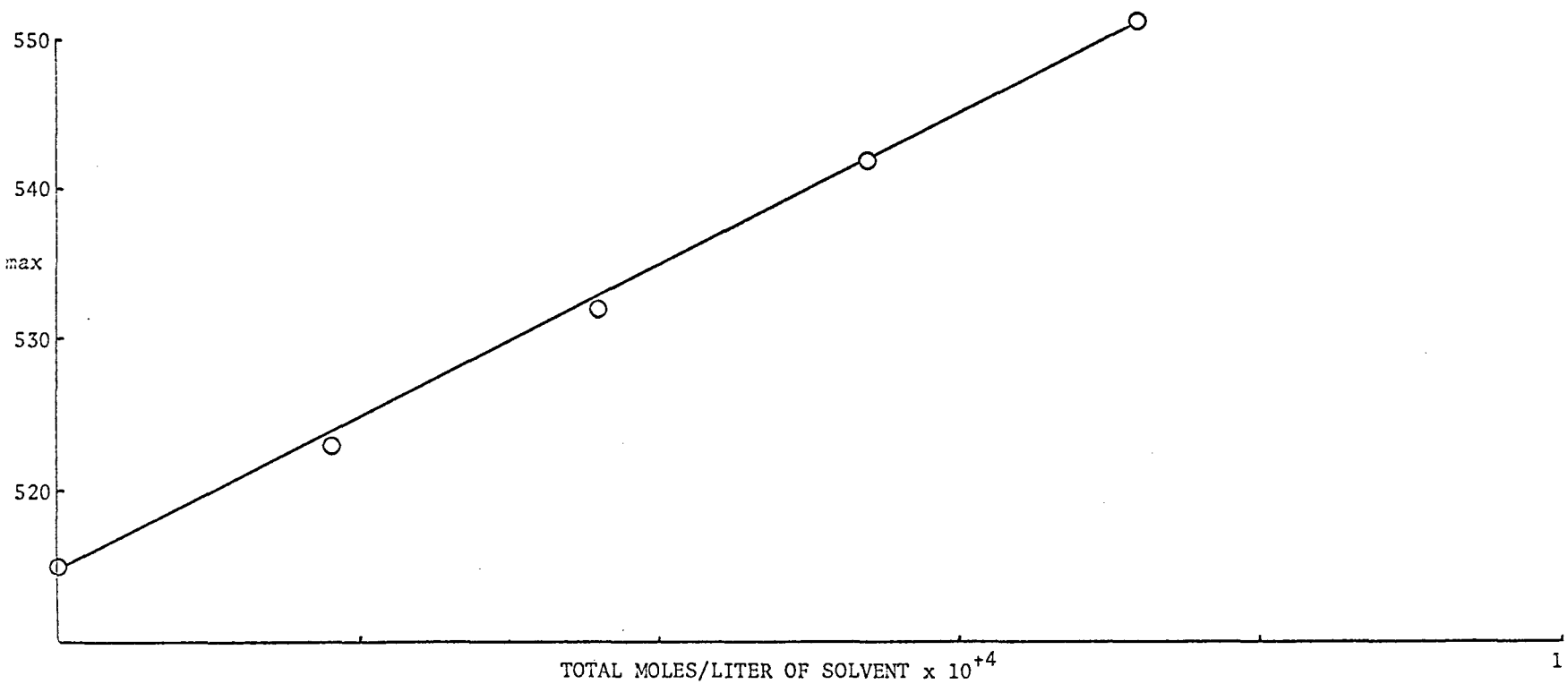


FIGURE 30

Solvent:n-HEXANE

76% (60-40 OCC-CN), 24% CCl

18°C

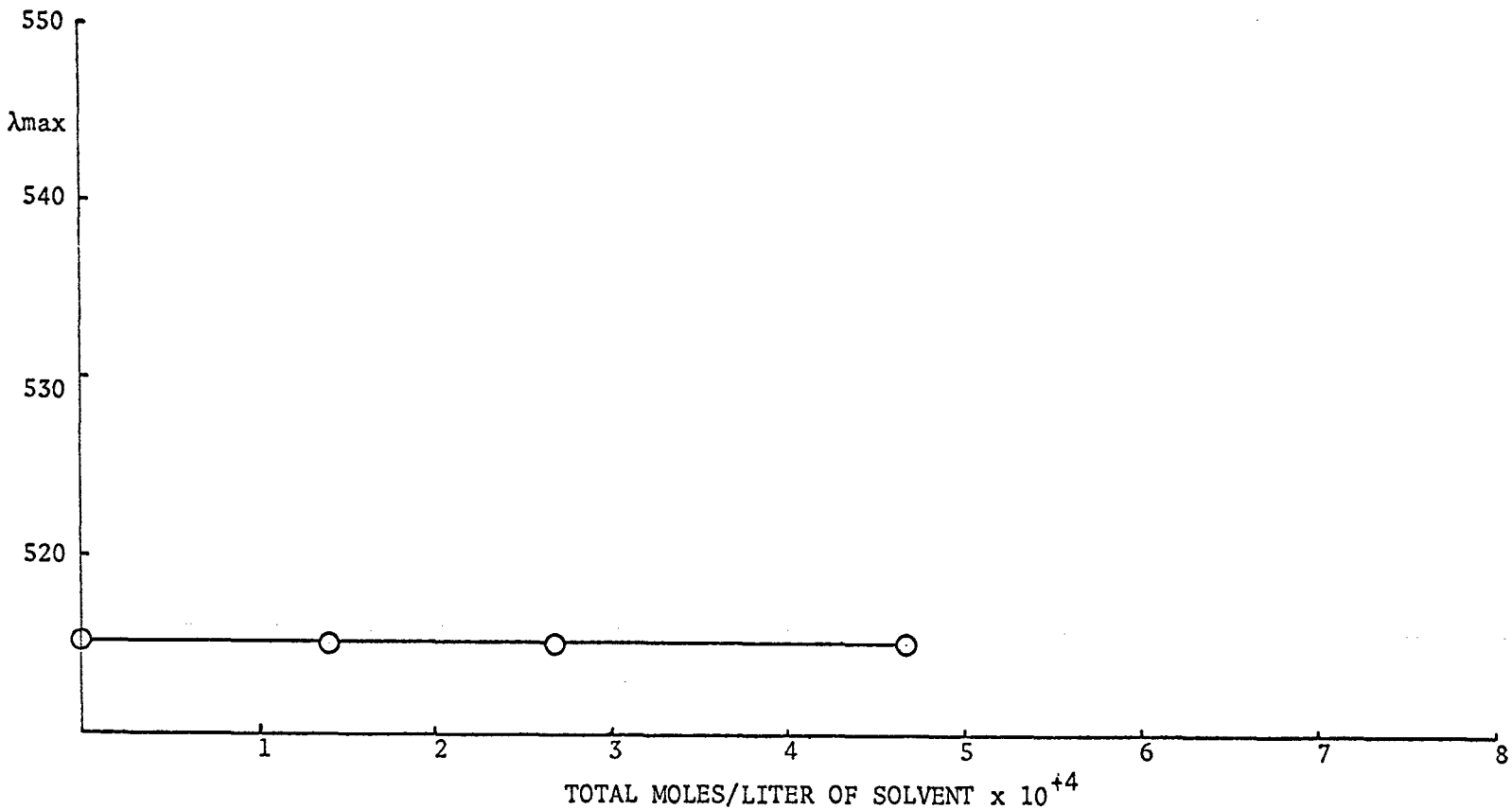


FIGURE 31

Solvent: CYCLOHEXANE

76% (60-40 OCC-CN), 24% CCl

18°C

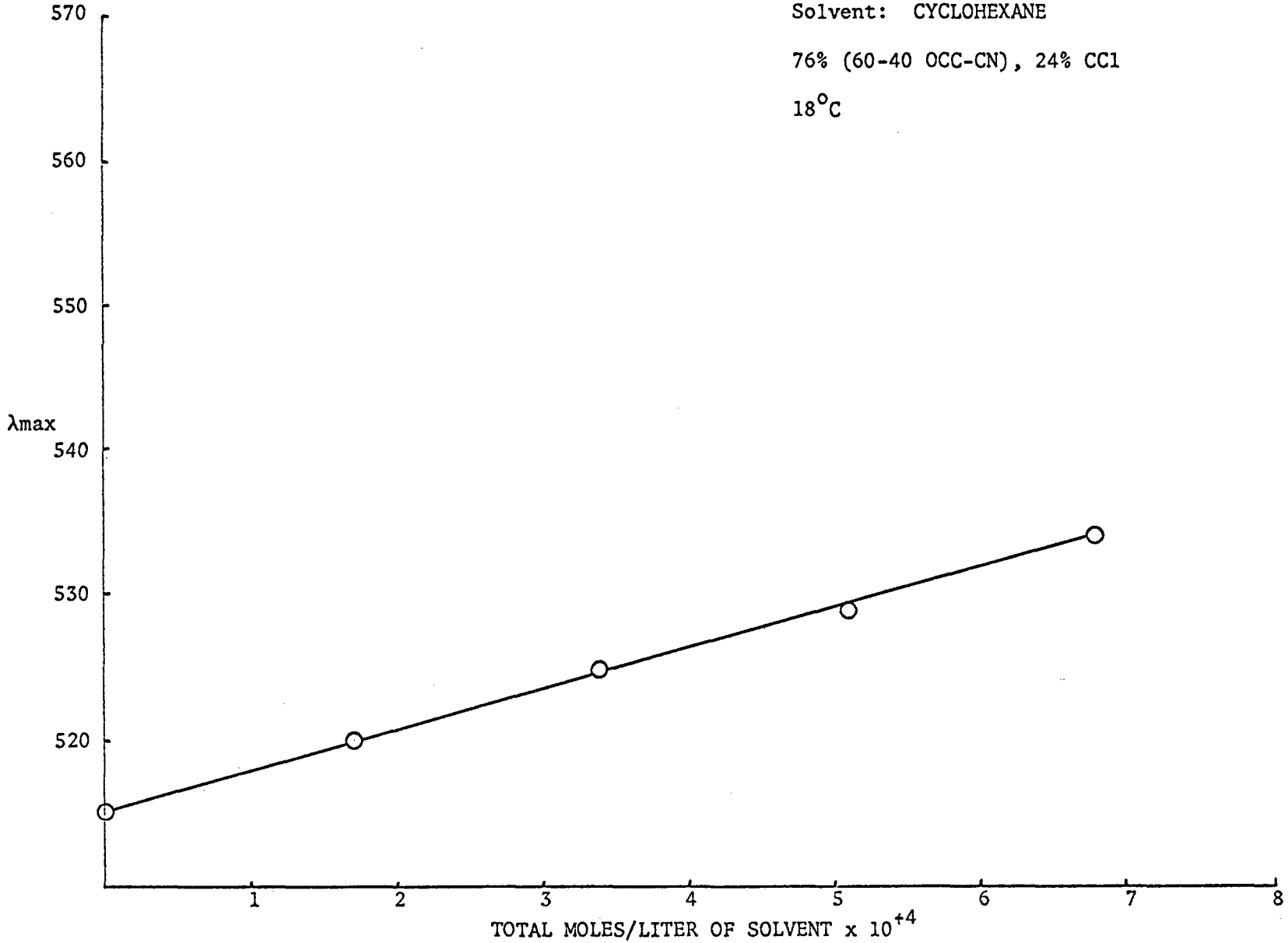


FIGURE 32

Solvent: METHYL CYCLOHEXANE

76% (60-40 OCC-CN), 24% CCl

18°C

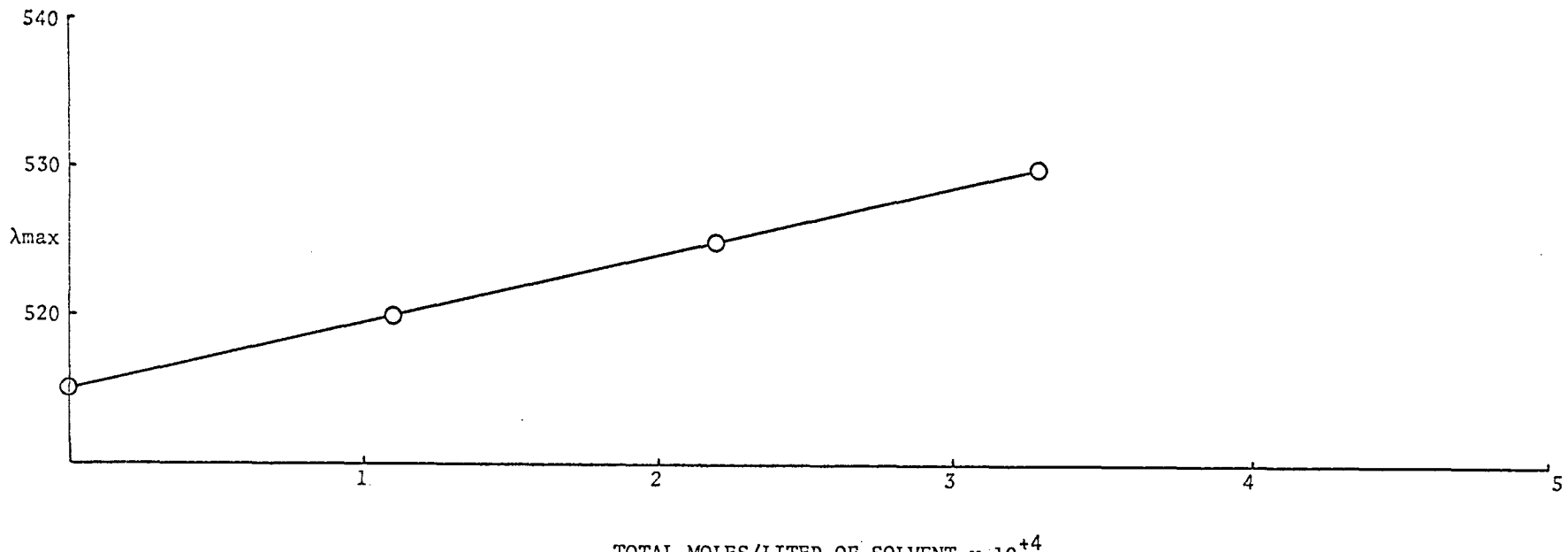
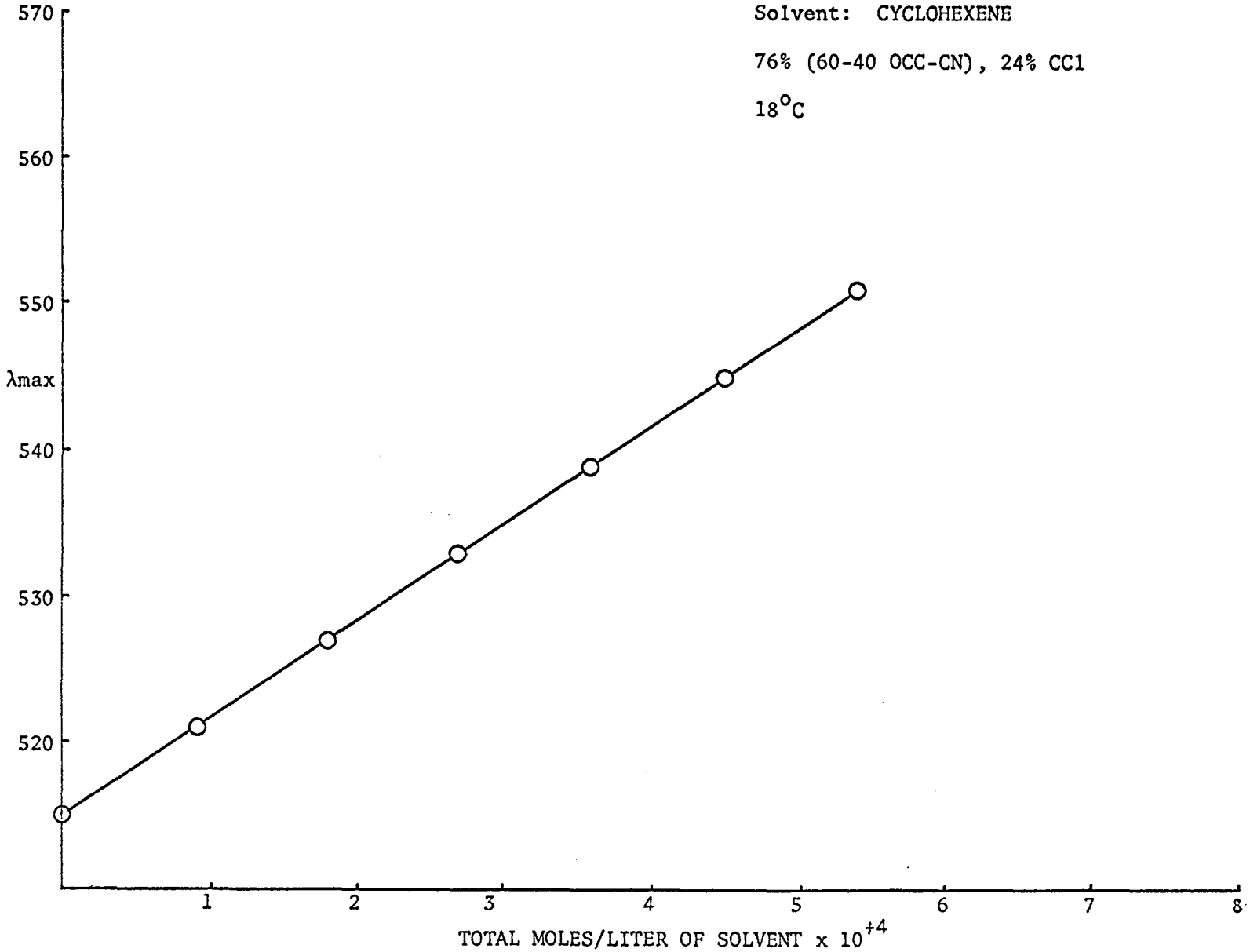


FIGURE 33

Solvent: CYCLOHEXENE

76% (60-40 OCC-CN), 24% CCl

18°C



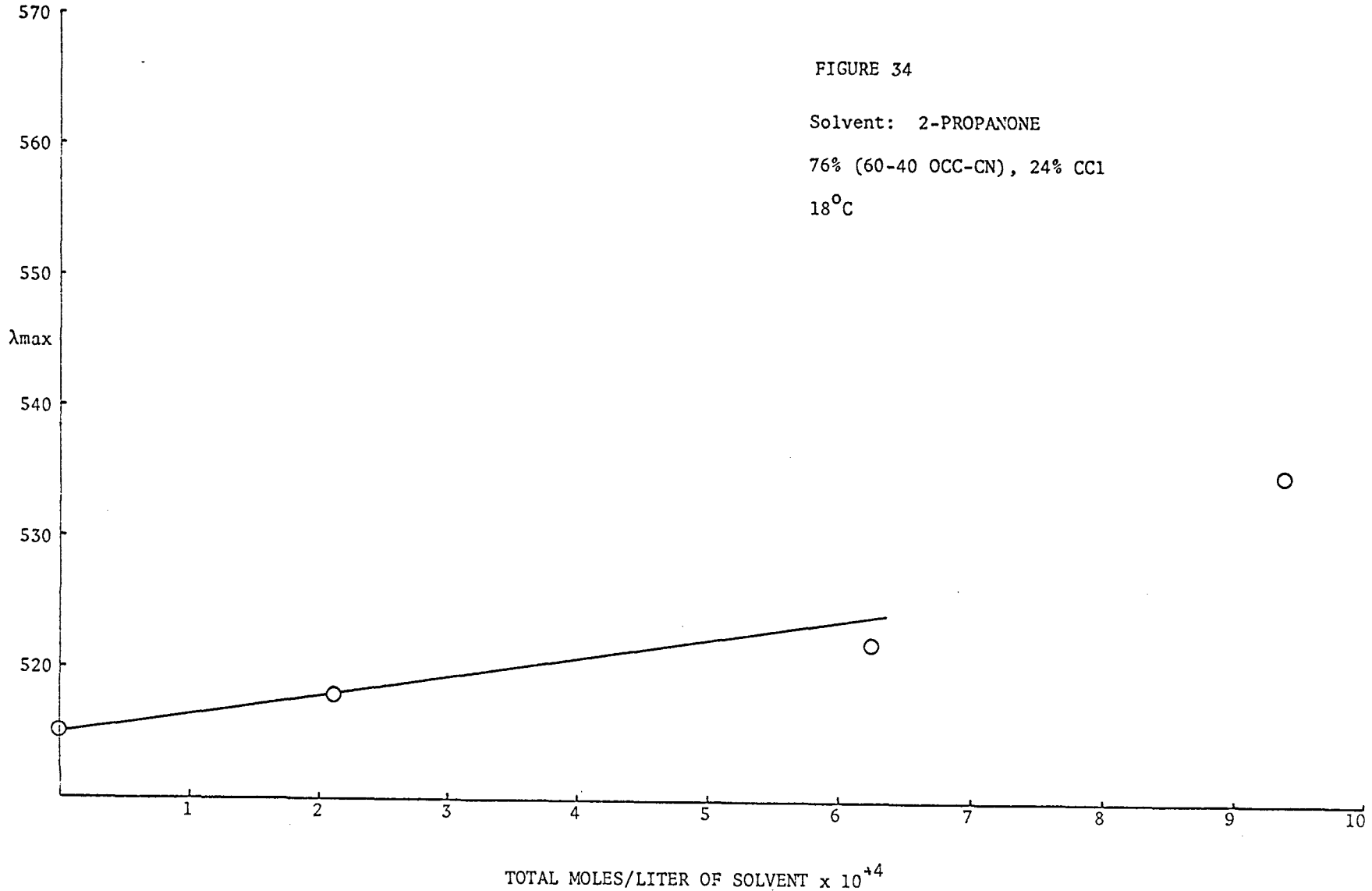


FIGURE 34

Solvent: 2-PROPANONE

76% (60-40 OCC-CN), 24% CCl

18°C

FIGURE 35

Solvent: 2-BUTANONE

76% (60-40 OCC-CN), 24% CCl

18°C

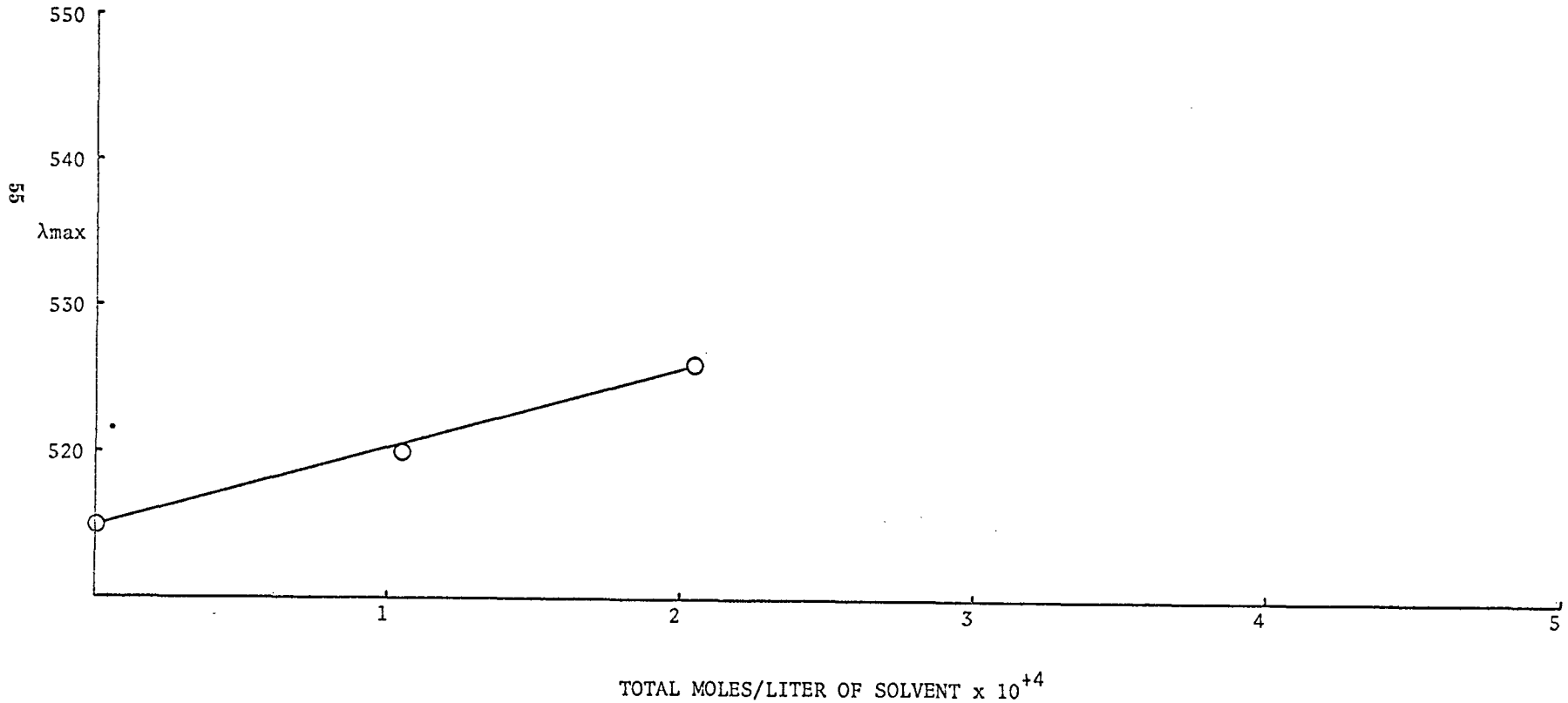


FIGURE 36

Solvent: 2-PENTANONE

76% (60-40 OCC-CN), 24% CCl

18°C

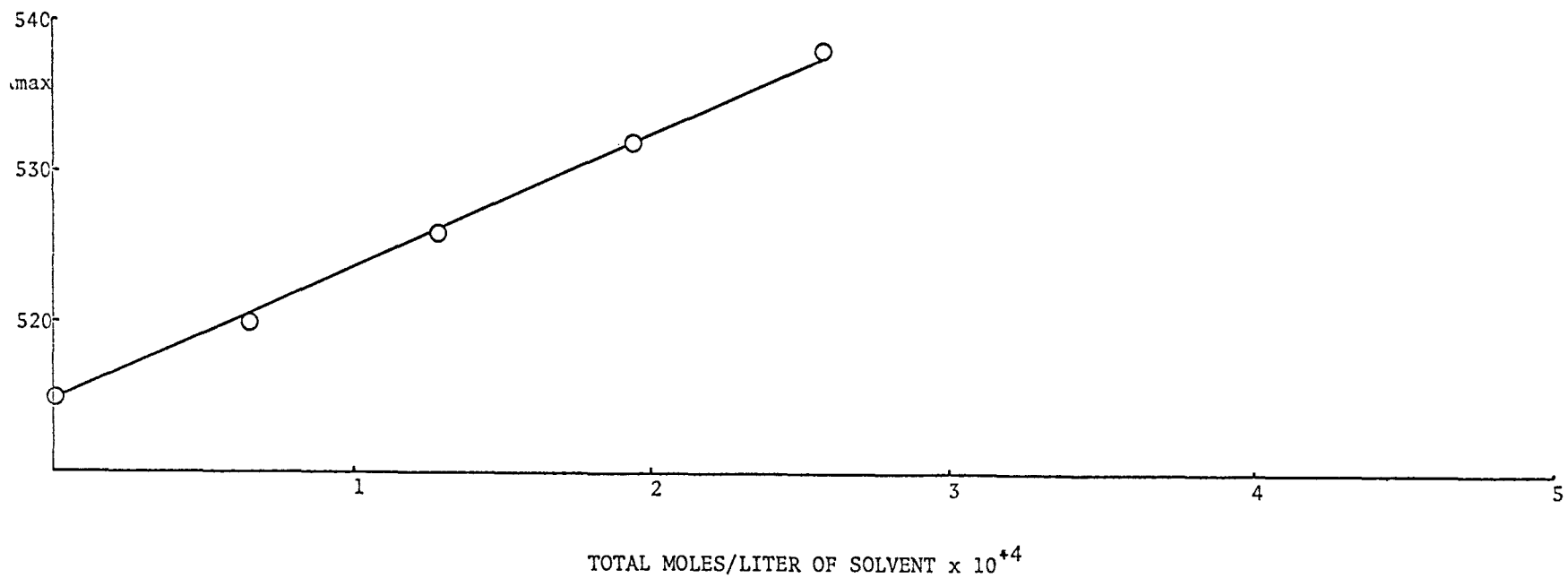


FIGURE 37

Solvent: 3-METHYL-2-BUTANONE

76% (60-40 OCC-CN), 24% CCl

18°C

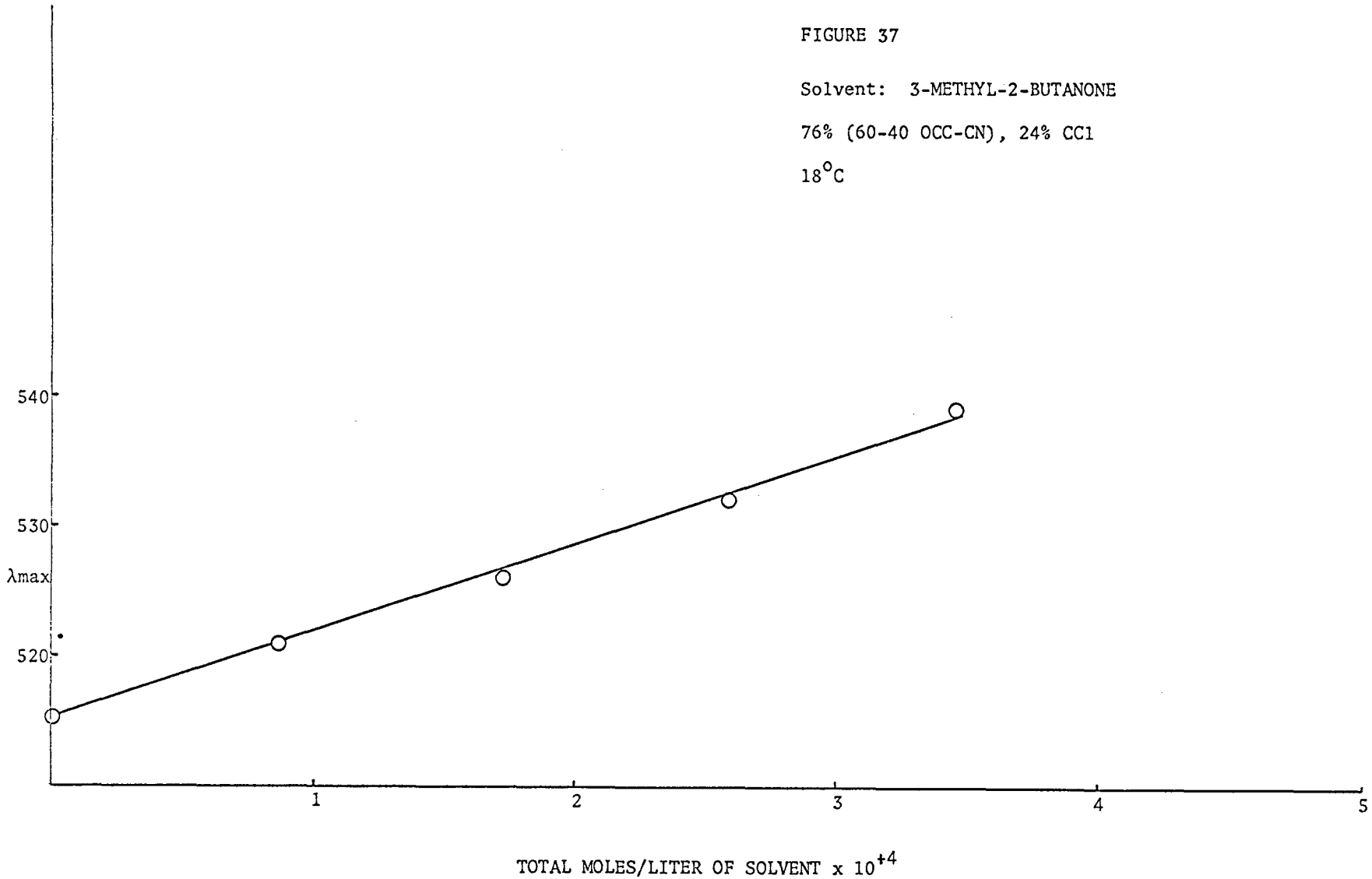


FIGURE 38

Solvent: METHANOL

76% (60-40 OCC-CN), 24% CCl

18°C

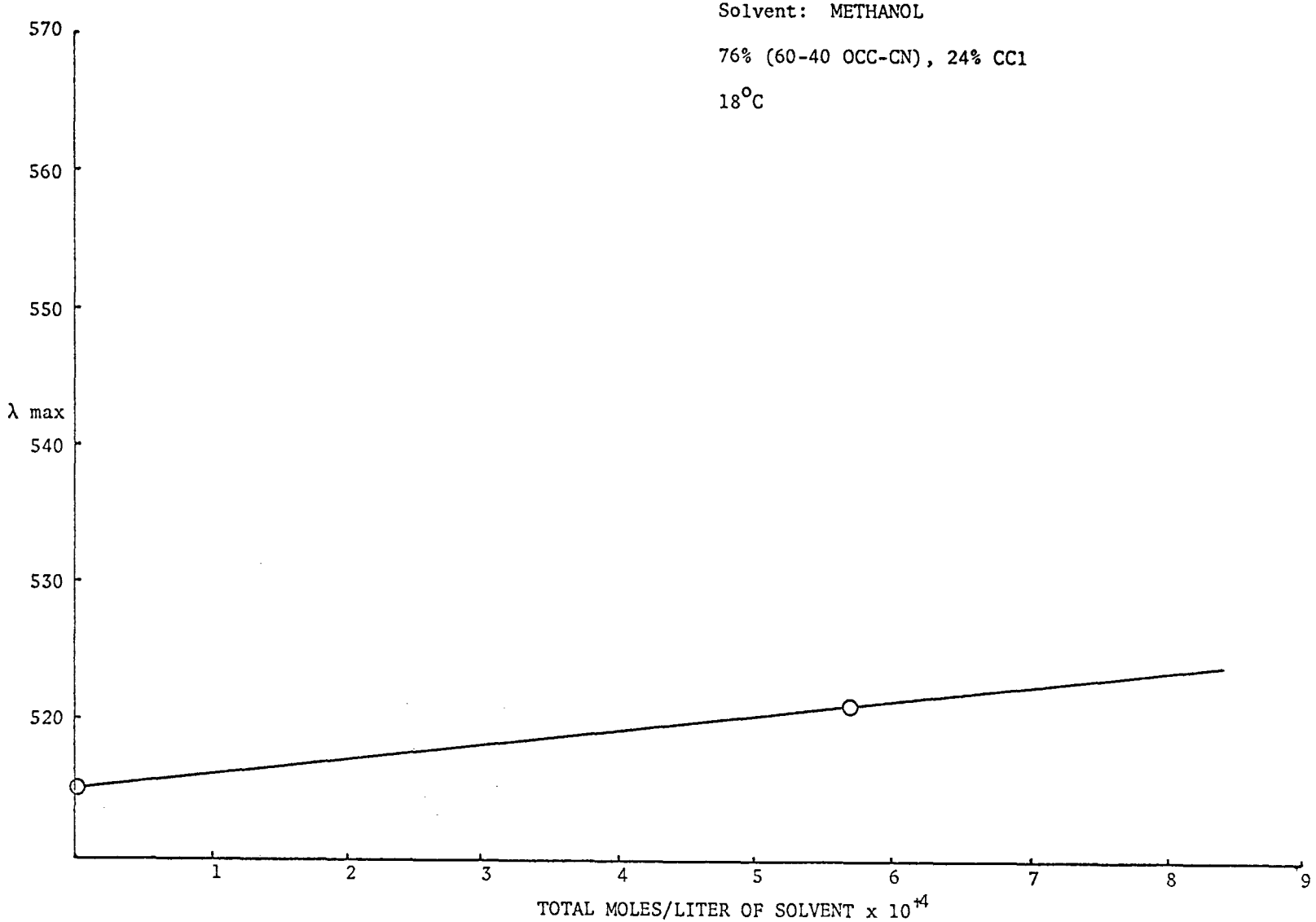


FIGURE 39

Solvent: ETHANOL

76% (60-40 OCC-CN), 24% CCl

18°C

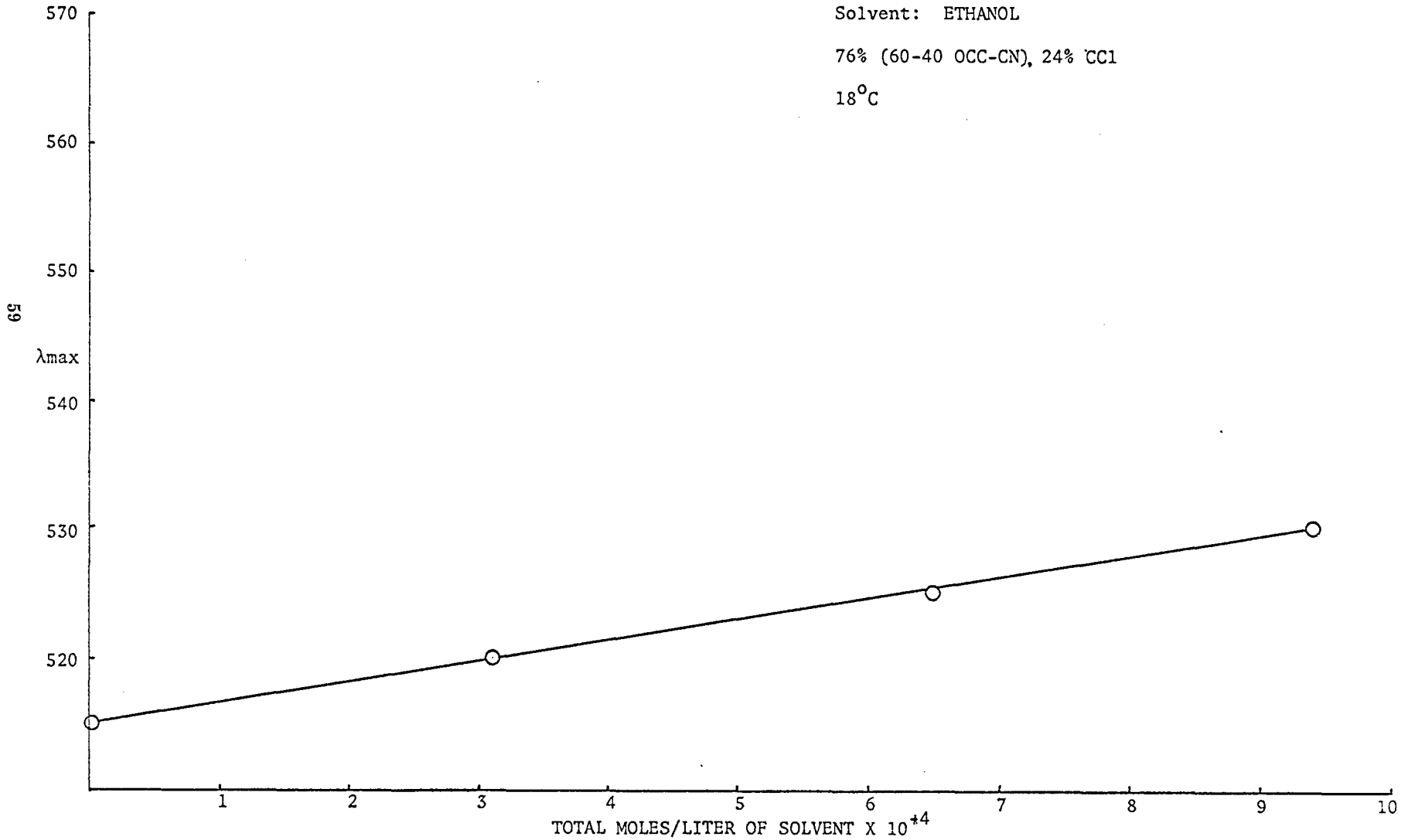


FIGURE 40

Solvent: 1-PROPANOL

76% (60-40 OCC-CN), 24% CCl

18°C

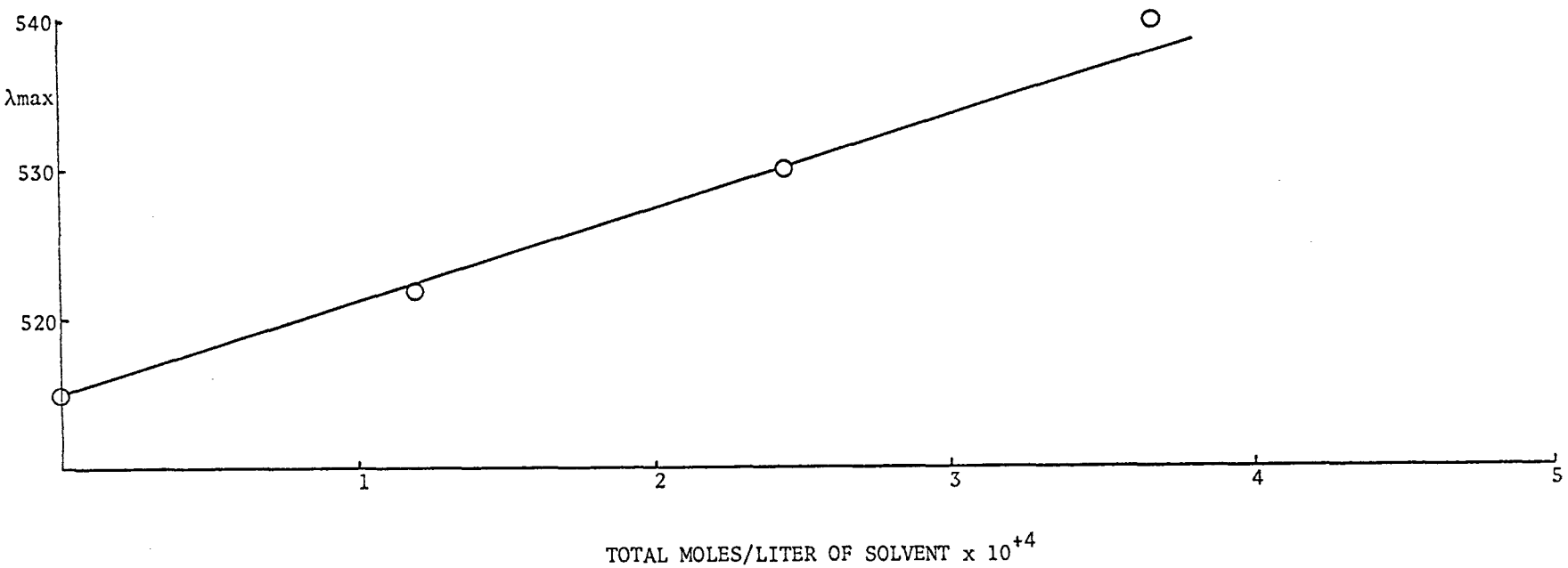


FIGURE 41

Solvent: 1-BUTANOL

76% (60-40 OCC-CN), 24% CCl

18°C

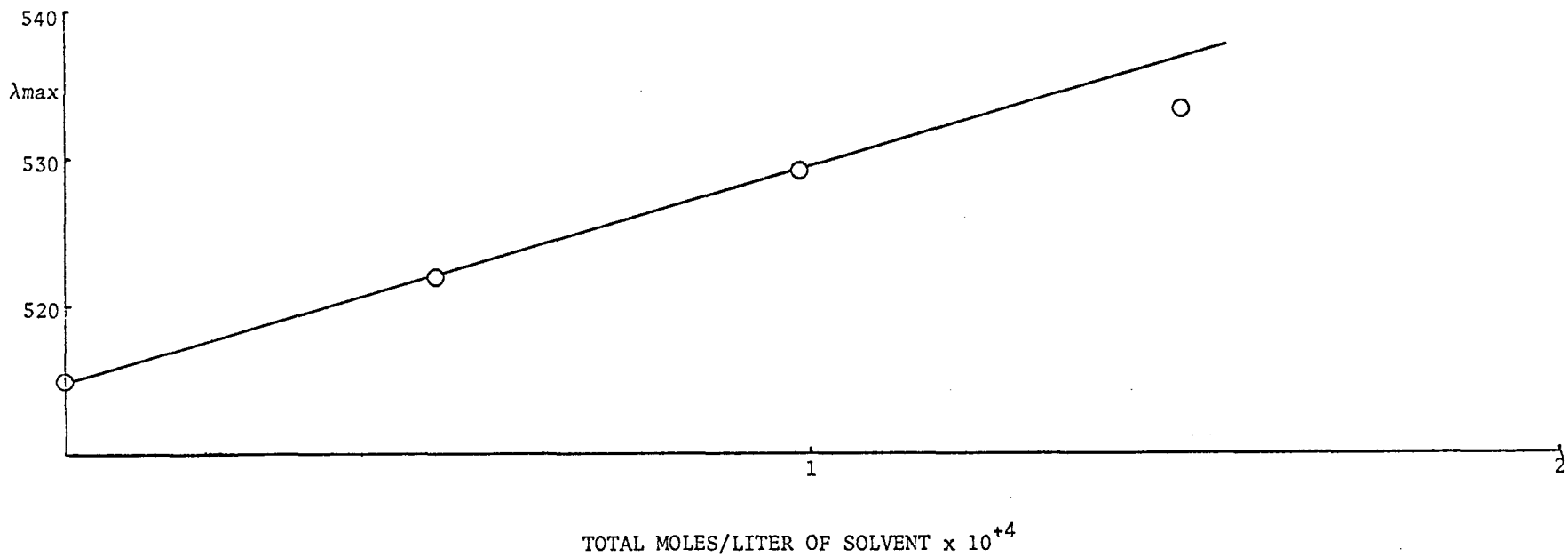


FIGURE 42

Solvent: 2-PROPANOL

76% (60-40 OCC-CN), 24% CCl

18°C

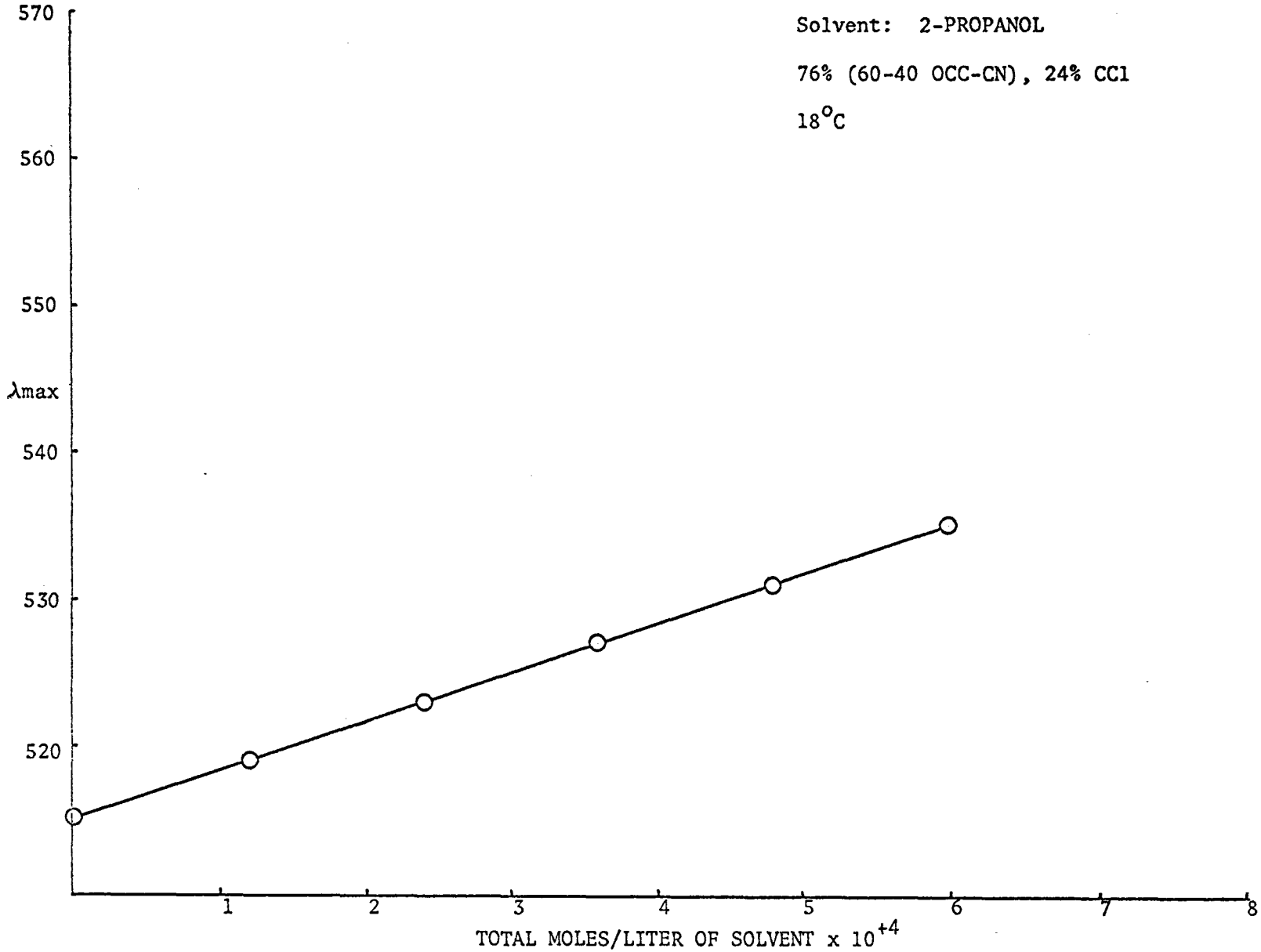


FIGURE 43

Solvent: 2-BUTANOL

76% (60-40 OCC-CN), 24% CCl

18°C

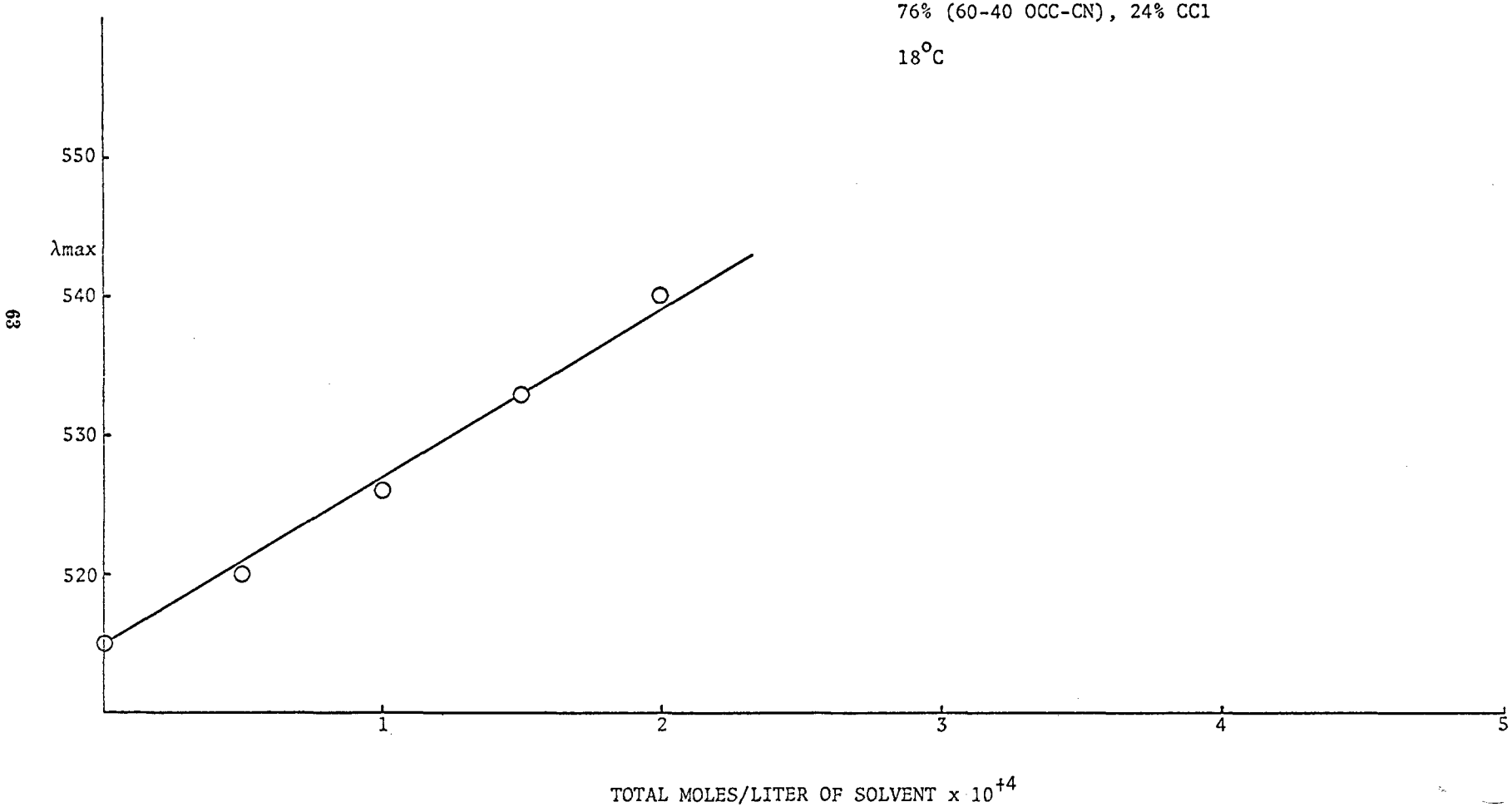


FIGURE 44

Solvent: METHYL ETHANONATE

76% (60-40 OCC-CN), 24% CCl

18°C

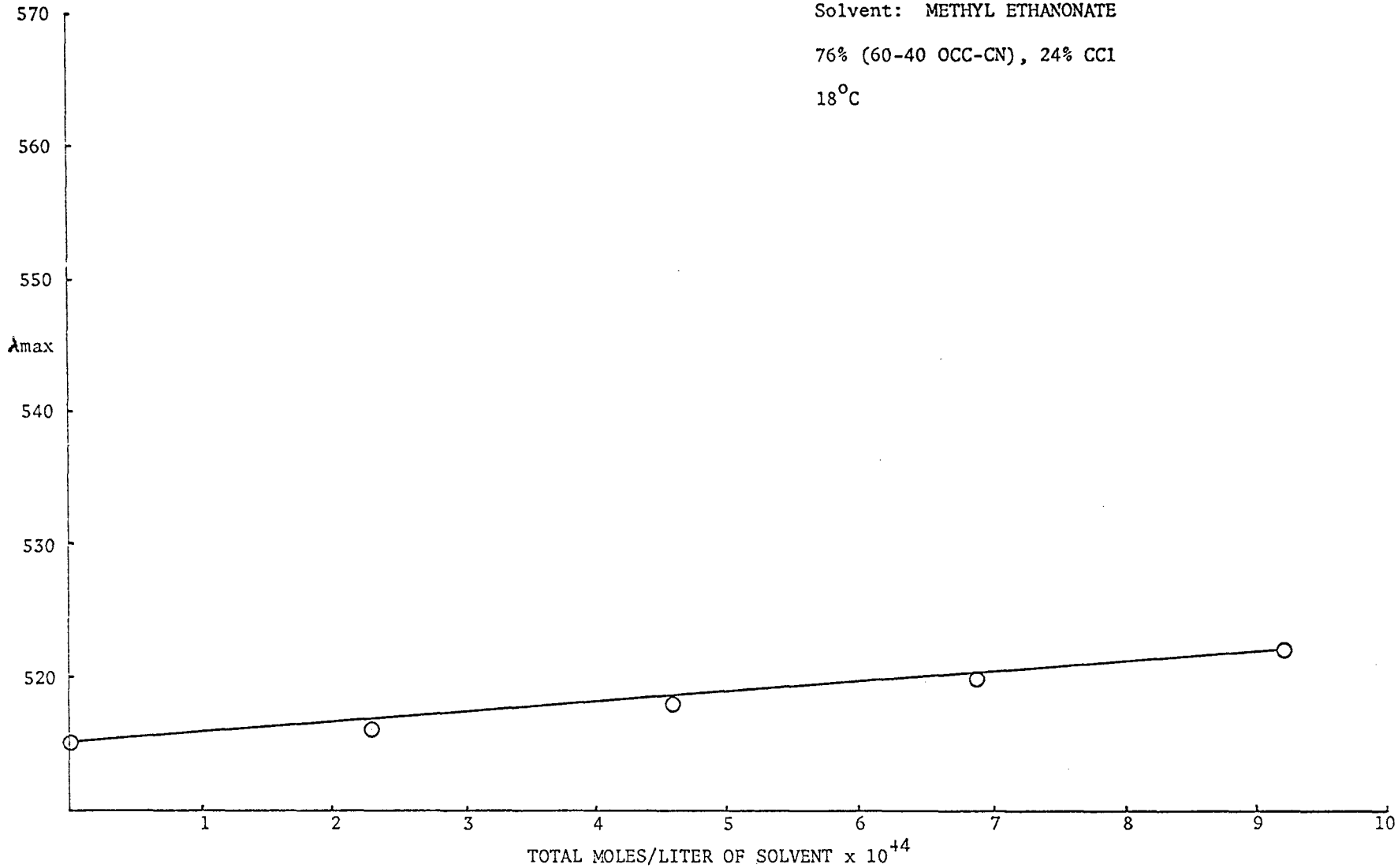


FIGURE 45

Solvent: ETHYL ETHANOATE

76% (60-40 OCC-CN), 24% CCl

18°C

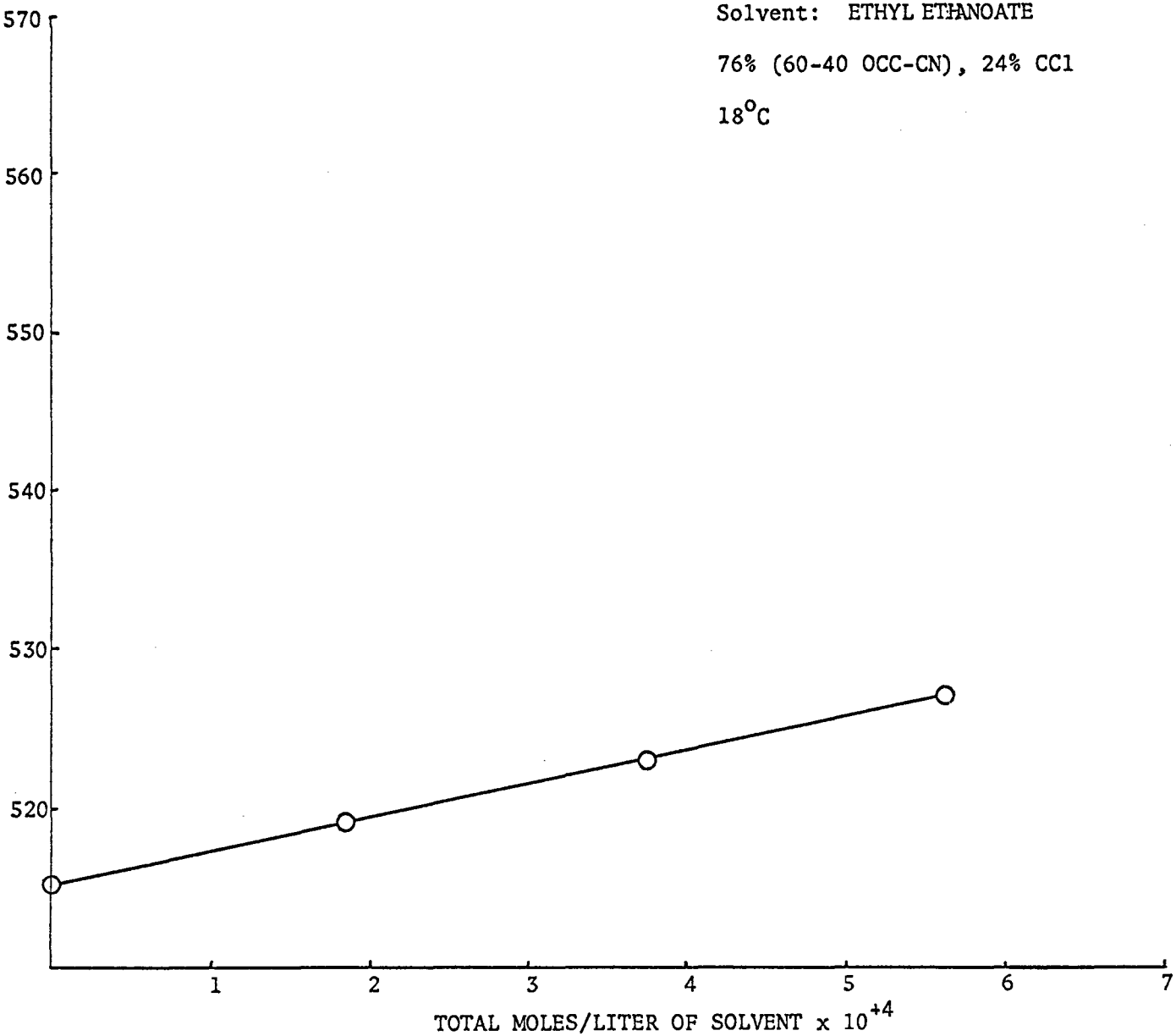


FIGURE 46

Solvent: PROPYL ETHANOATE

76% (60-40 OCC-CN), 24% CCl

18°C

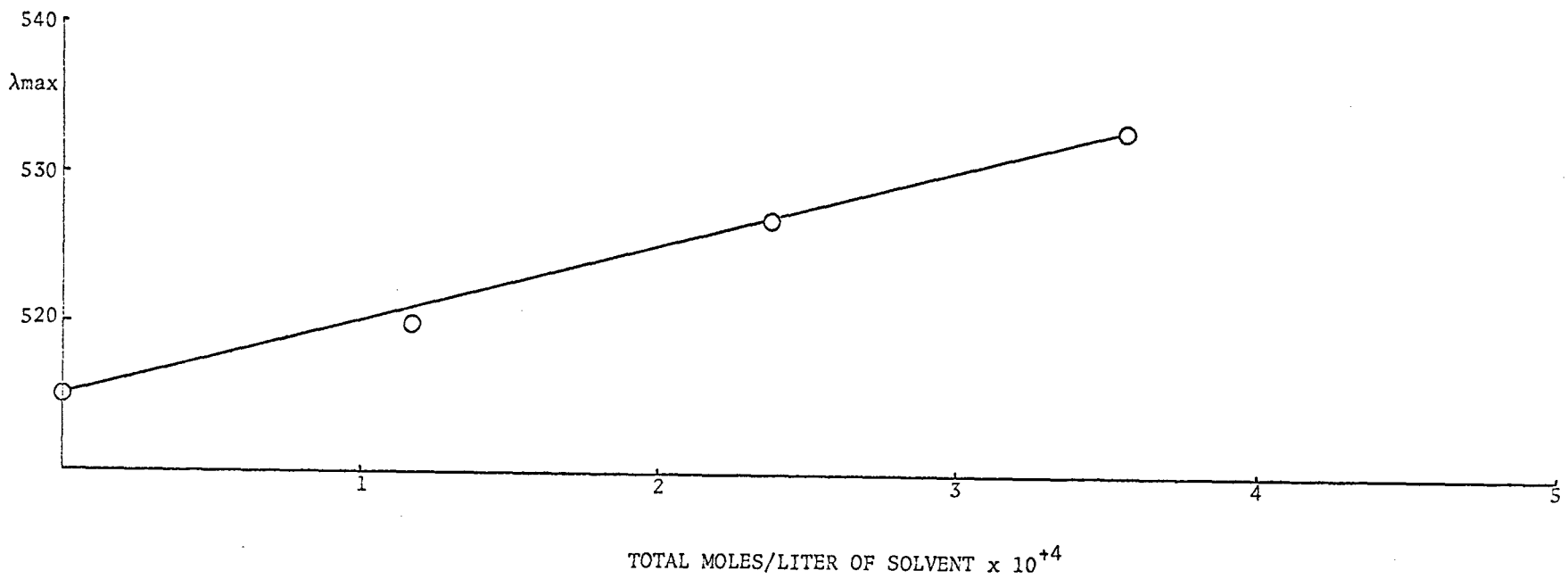


FIGURE 47

Solvent: METHYL PROPANOATE

76% (60-40 OCC-CN), 24% CCl

18°C

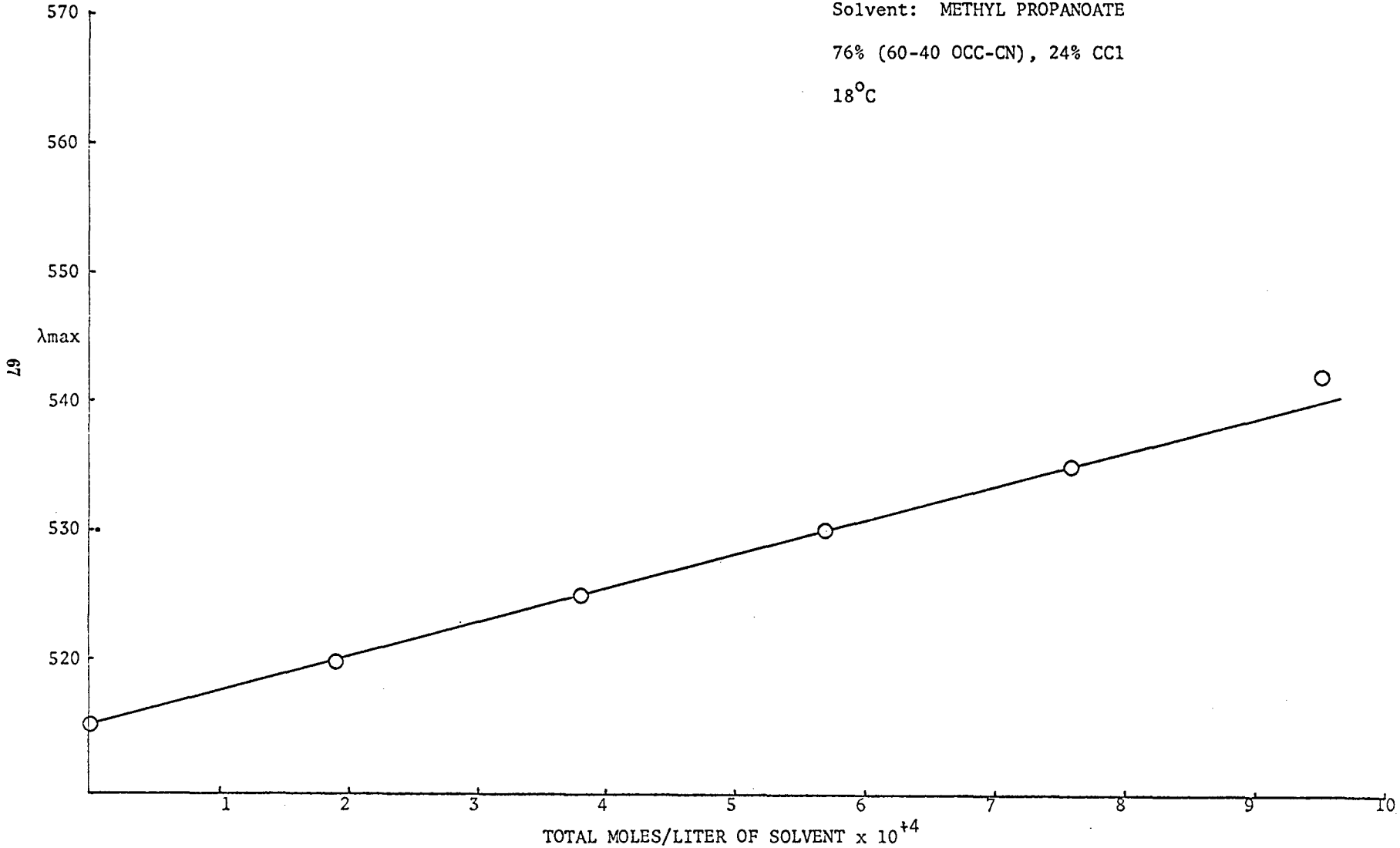


FIGURE 48

Solvent: METHYL BUTANOATE

76% (60-40 OCC-CN), 24% CCl

18°C

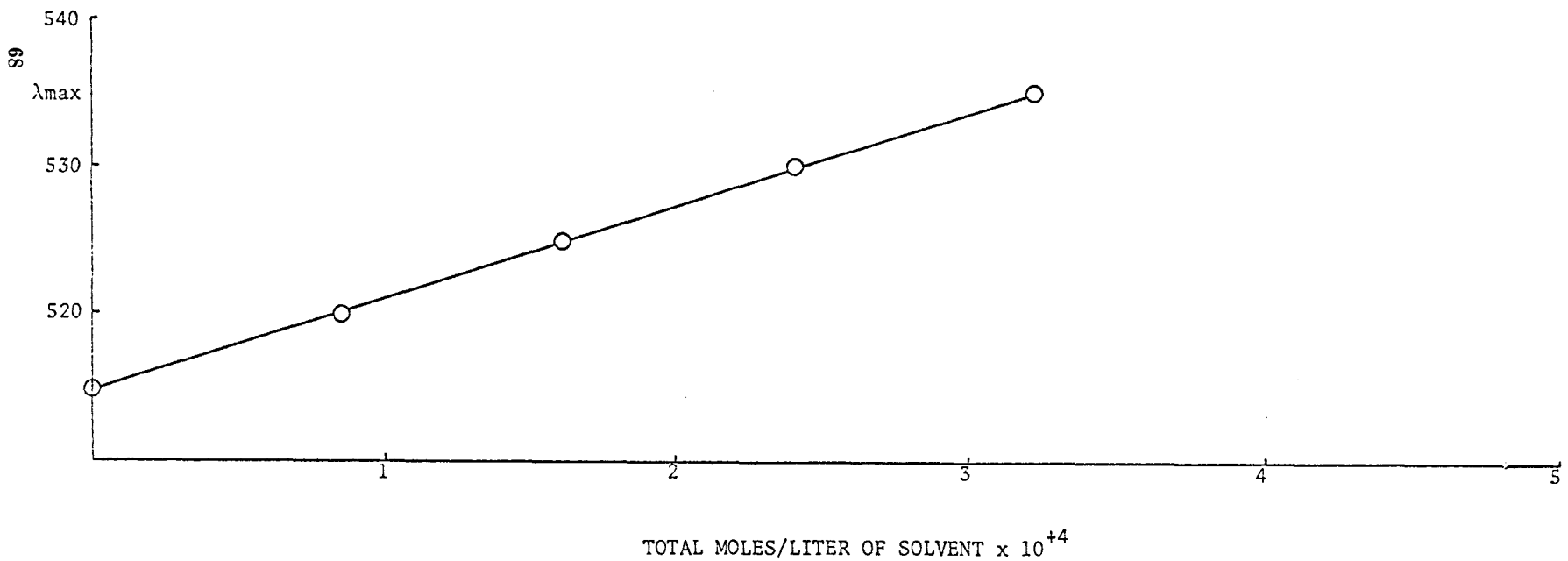


FIGURE 49

Solvent: ETHYL PROPIONATE

76% (60-40 OCC-CN), 24% CCl

18°C

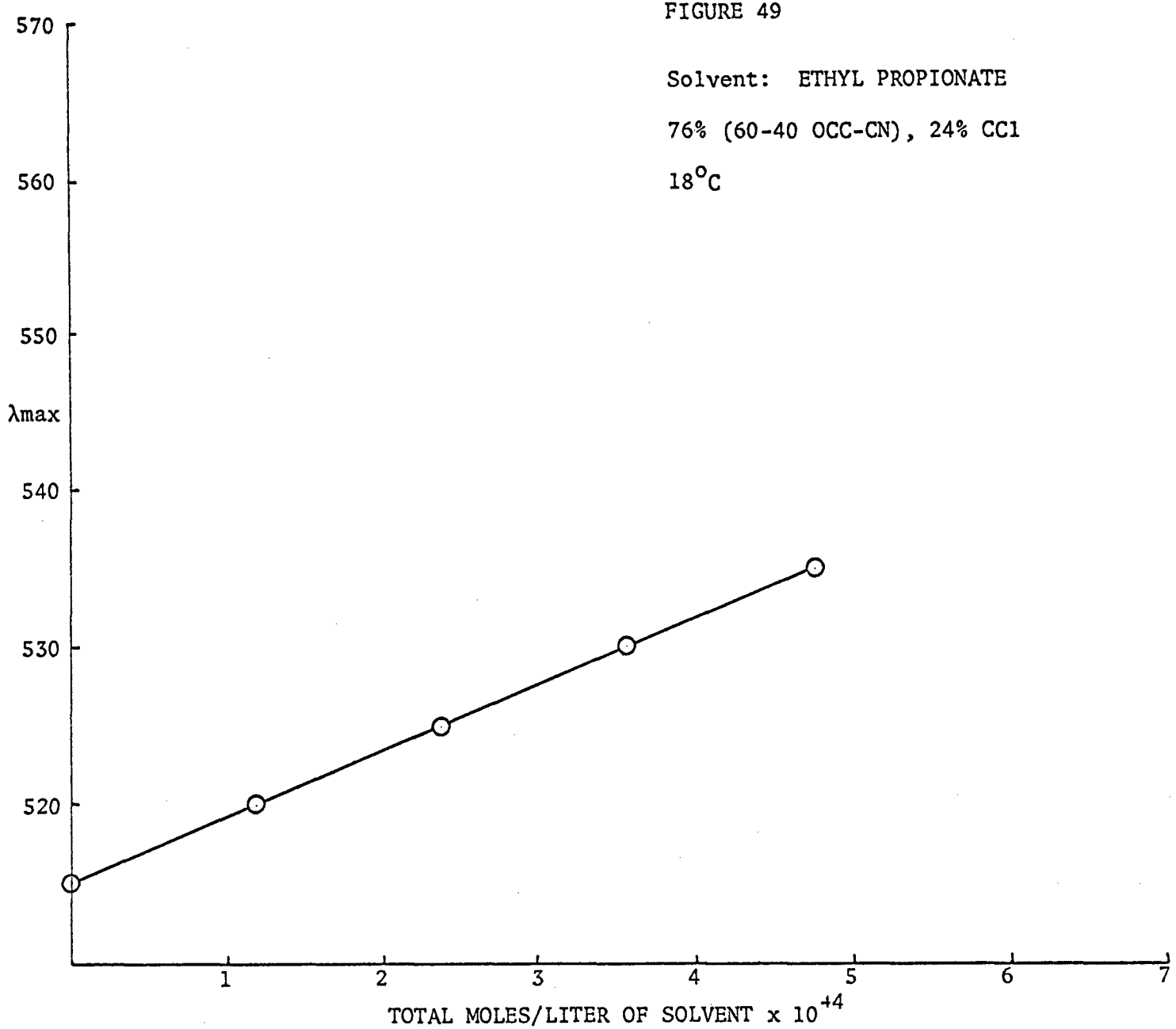


FIGURE 50

Solvent: α-METHYL-ETHYLETANOATE

76% (60-40 OCC-CN), 24% CCl

18°C

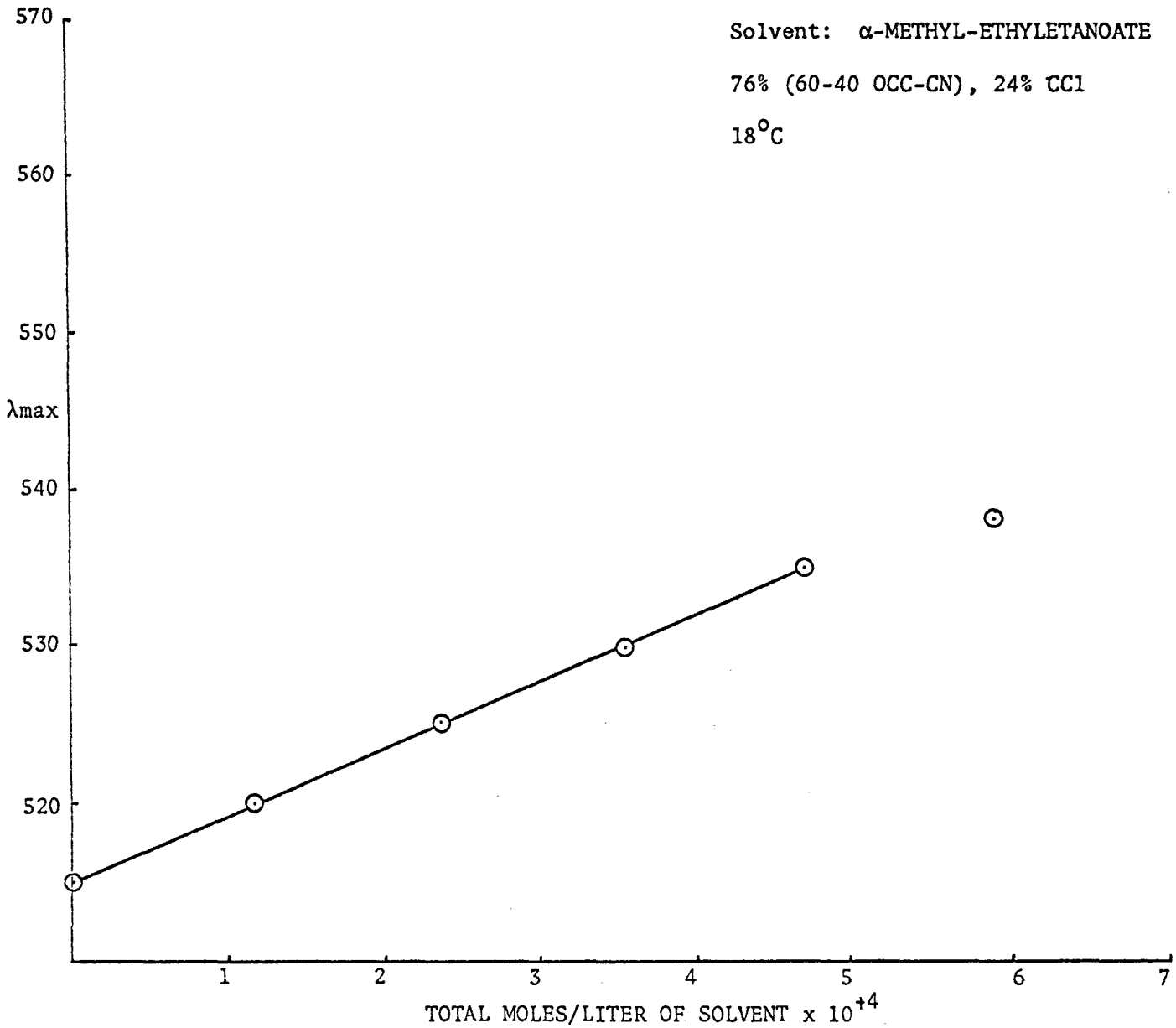


FIGURE 51

Solvent: METHYL 2-METHYLPROPANOATE

76% (60-40 OCC-CN), 24% CCl

18°C

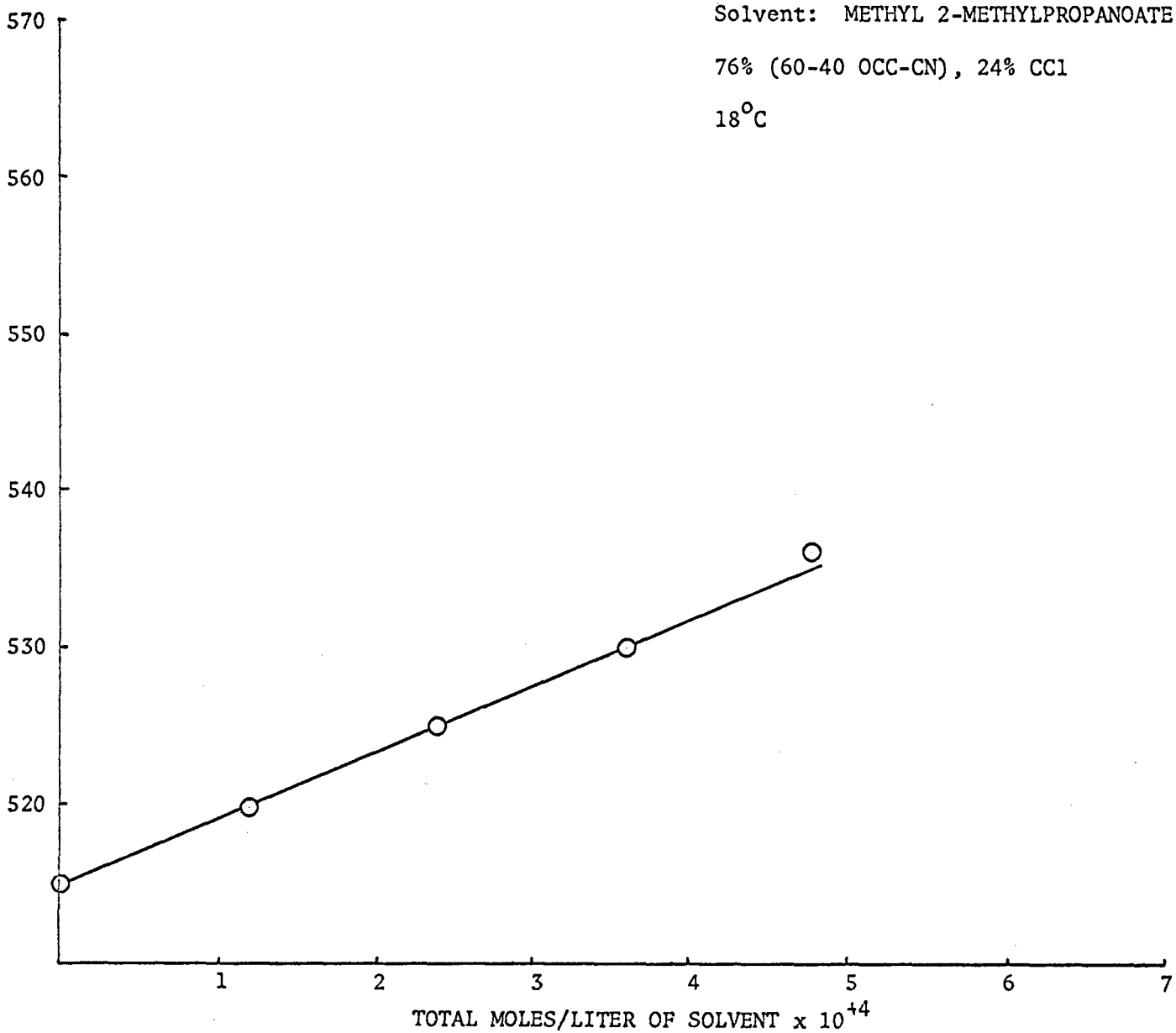


FIGURE 52

Solvent: DICHLOROMETHANE

74% (60-40 OCC-CN), 26% CCl

18°C

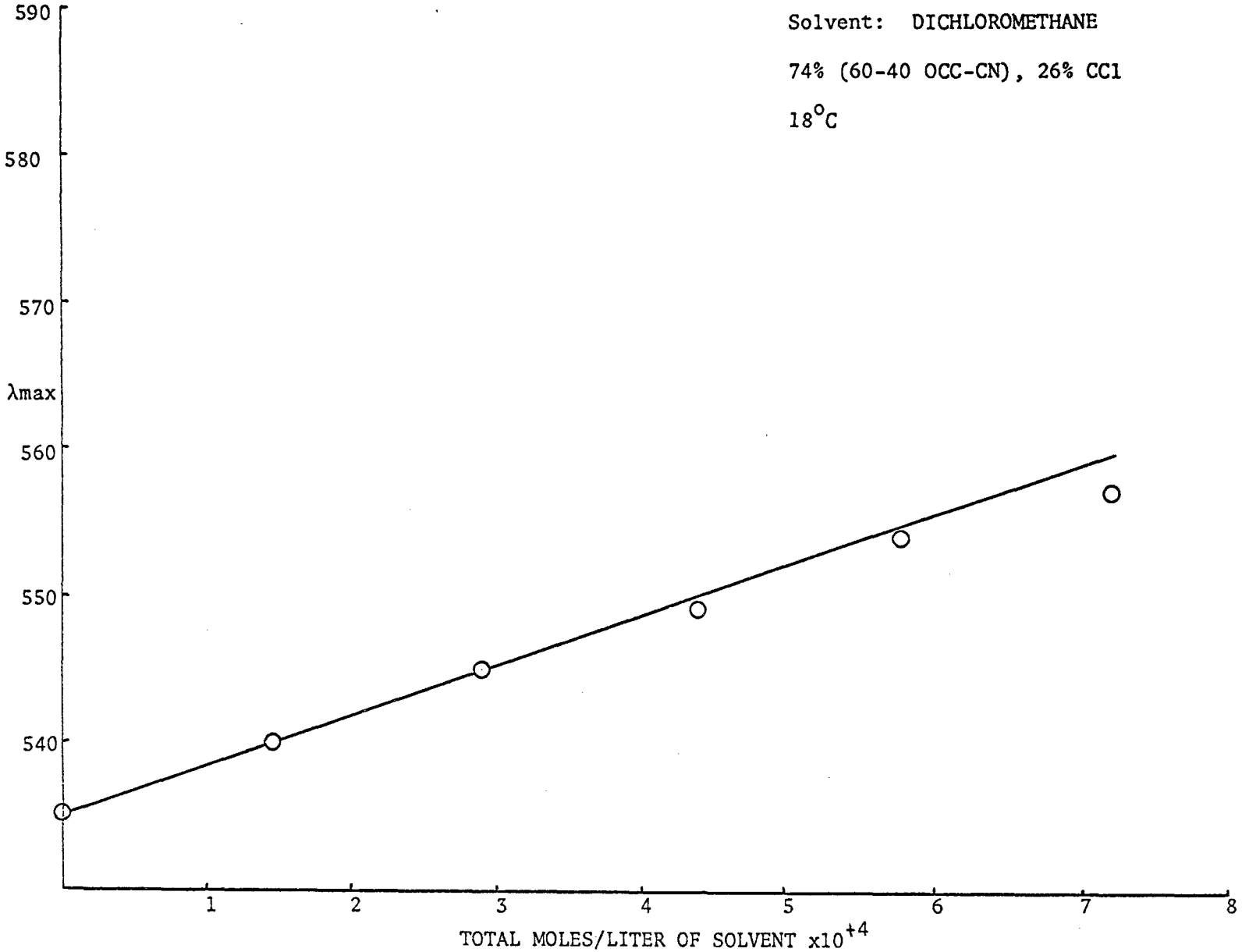


FIGURE 53

Solvent: CHLOROFORM

74% (60-40 OCC-CN), 26% CCl

18°C

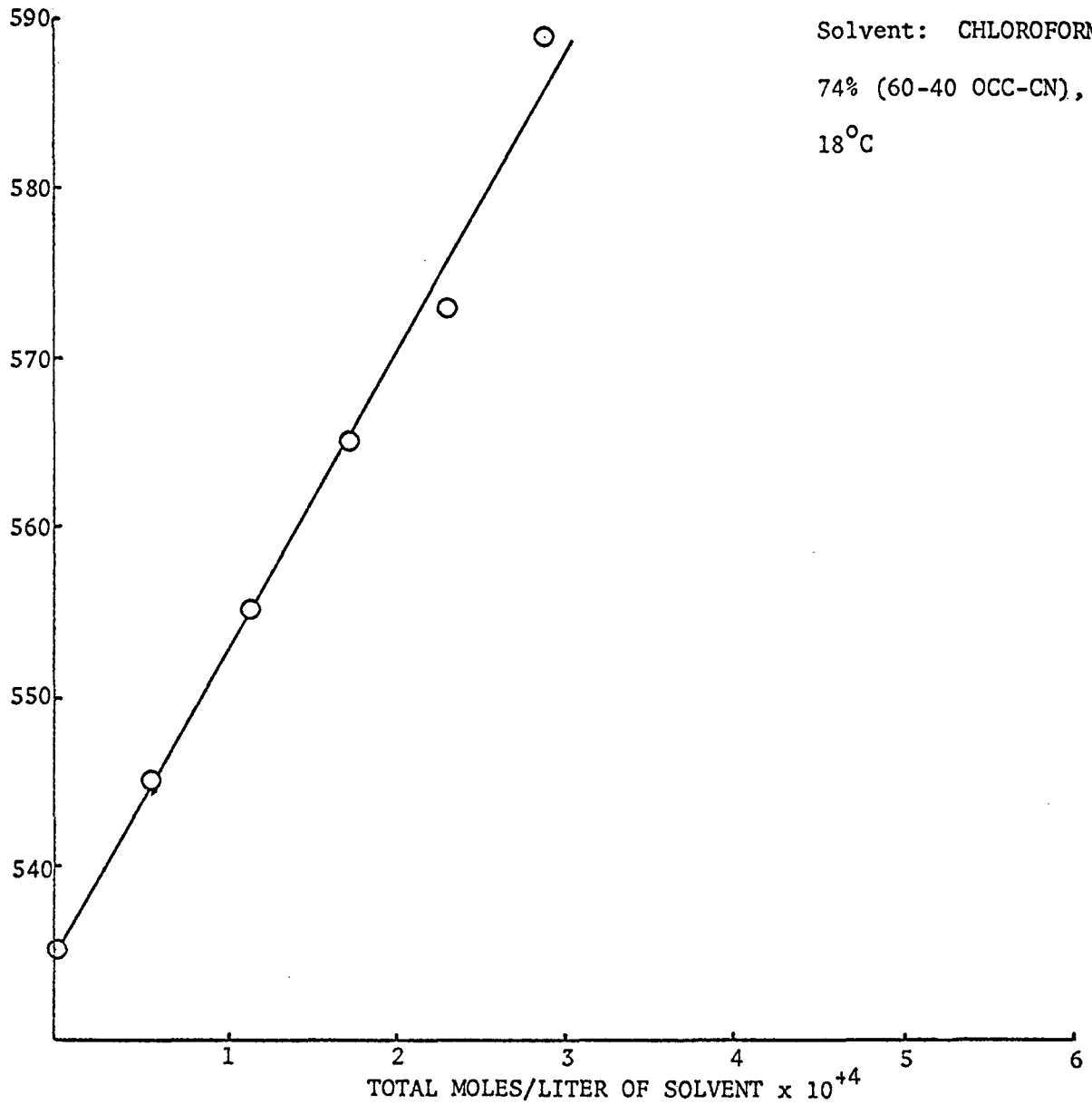


FIGURE 54

Solvent: CARBON TETRACHLORIDE

74% (OCC-CN), 26% CCl
(60-40)

18°C

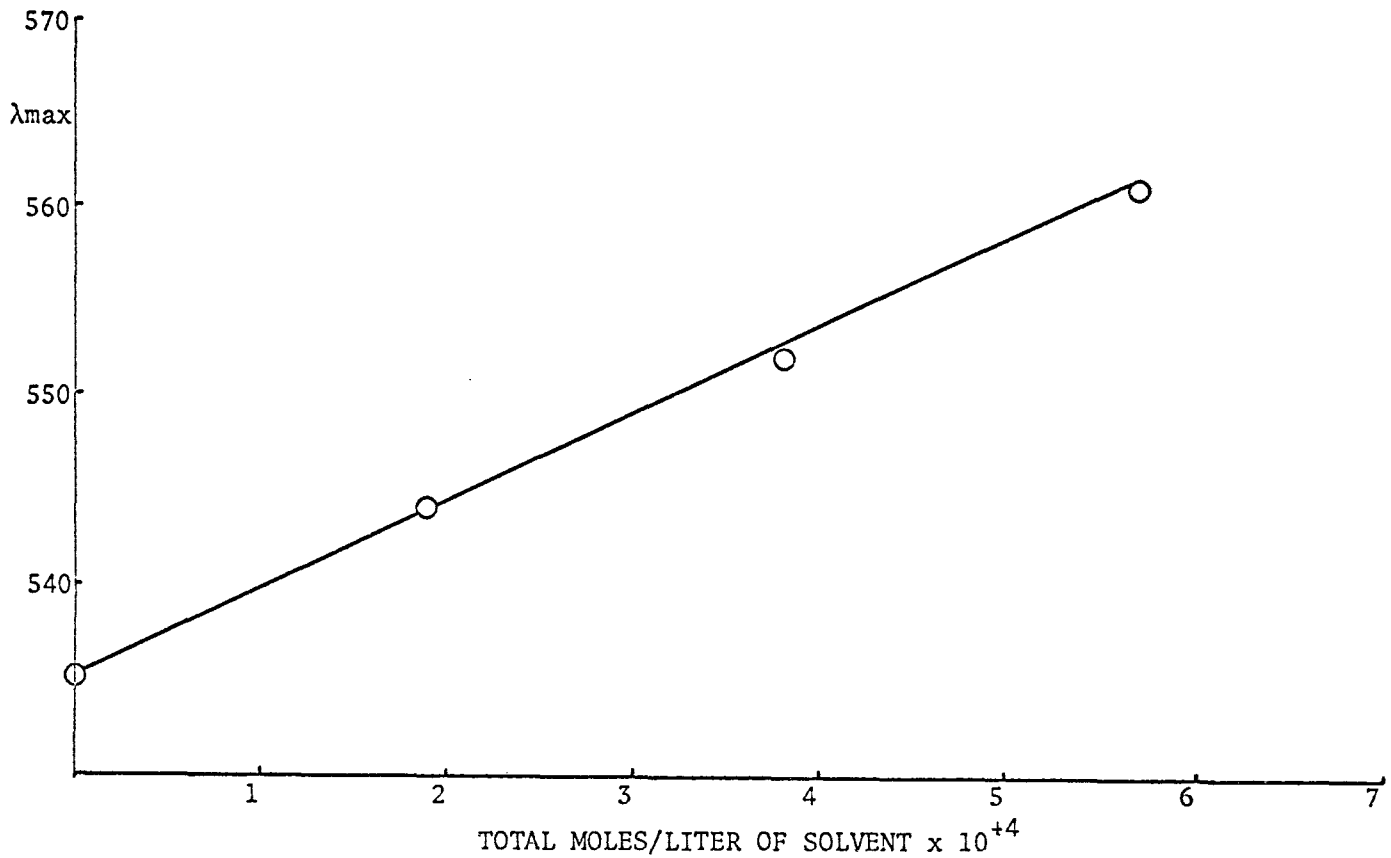


FIGURE 55

Solvent: BENZENE

74% (60-40 OCC-CN), 26% $\dot{C}Cl$

18°C

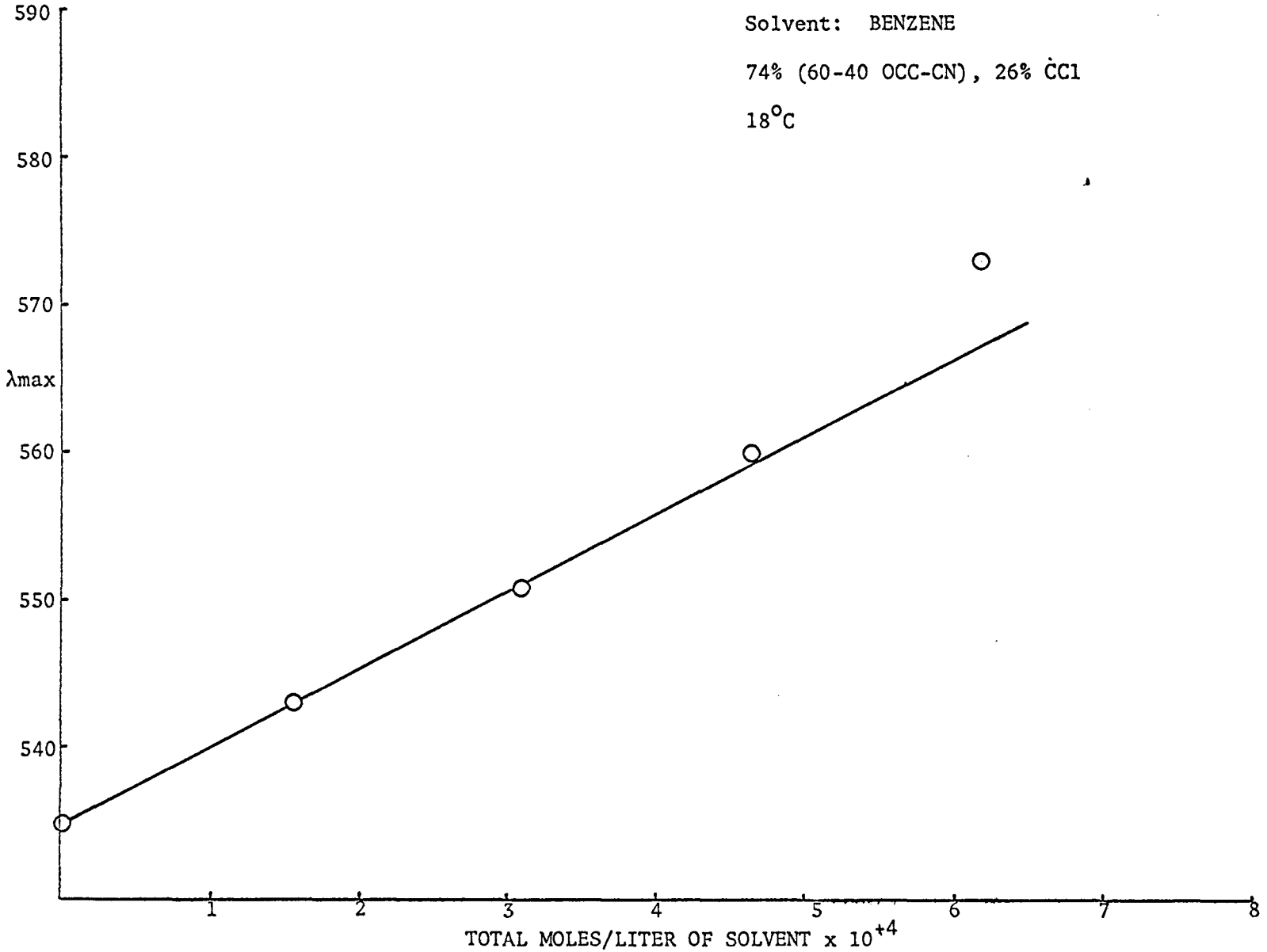


FIGURE 56

Solvent: o-XYLENE

74% (60-40 OCC-CN), 26% CCl

18°C

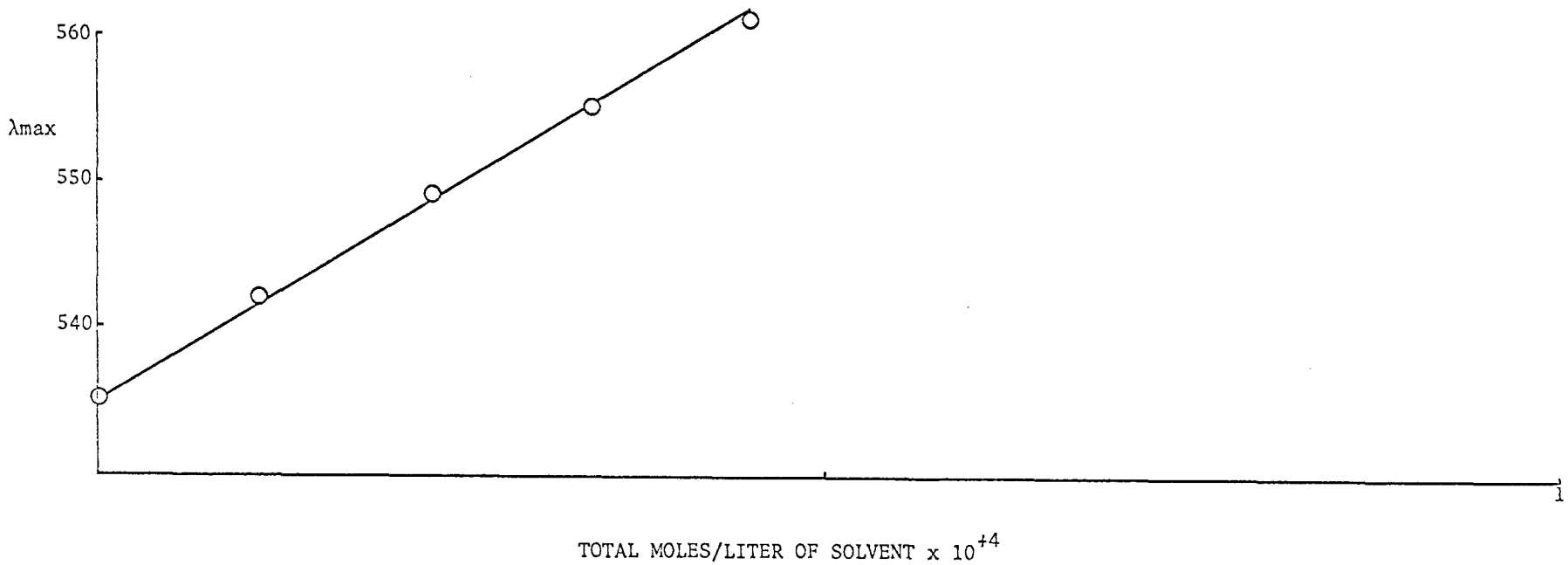


FIGURE 57

Solvent: m-XYLENE

74% (60-40 OCC-CN), 26% CCl

18°C

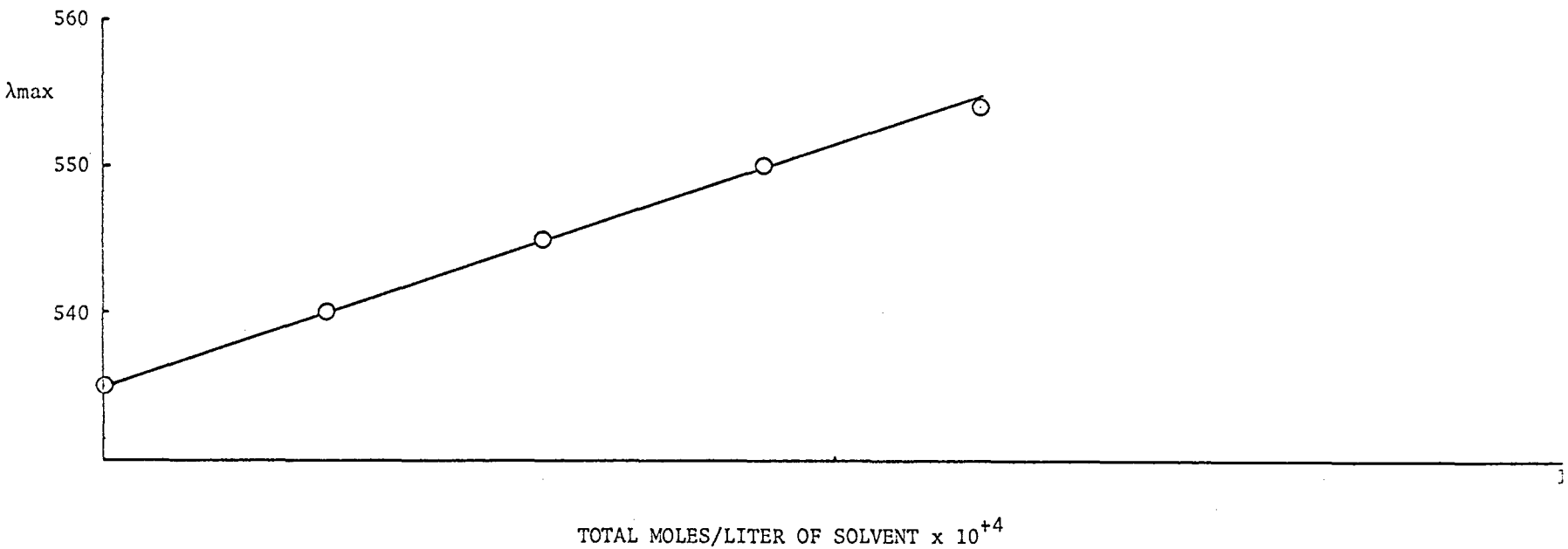
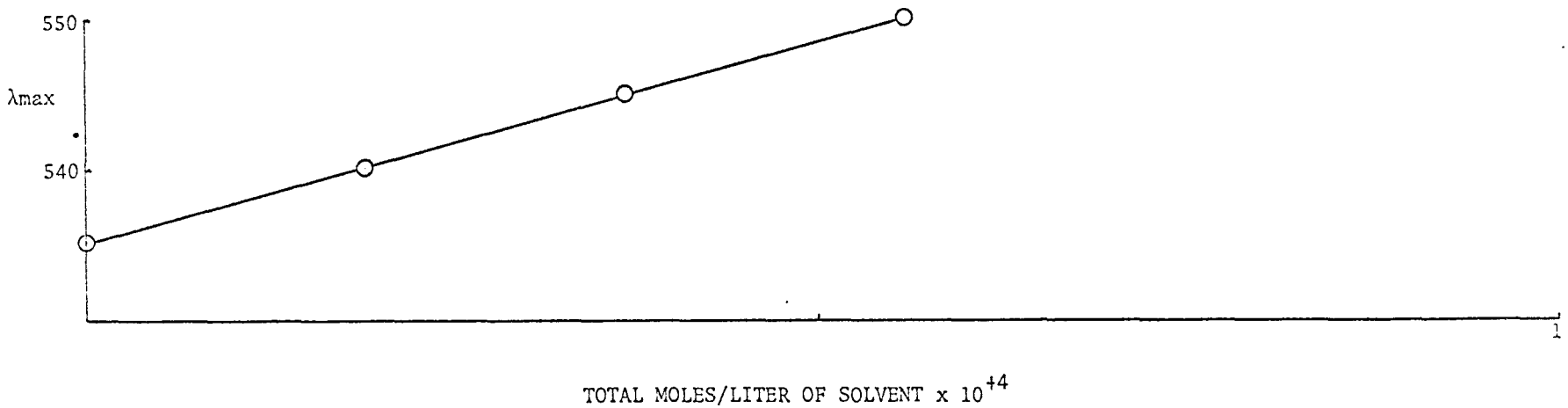


FIGURE 58

Solvent: p-XYLENE

74% (60-40 OCC-CN), 26% CCl

18°C



TOTAL MOLES/LITER OF SOLVENT x 10^{+4}

FIGURE 59

Solvent: n-HEXANE

74% (60-40 OCC-CN), 26% CCl

18°C

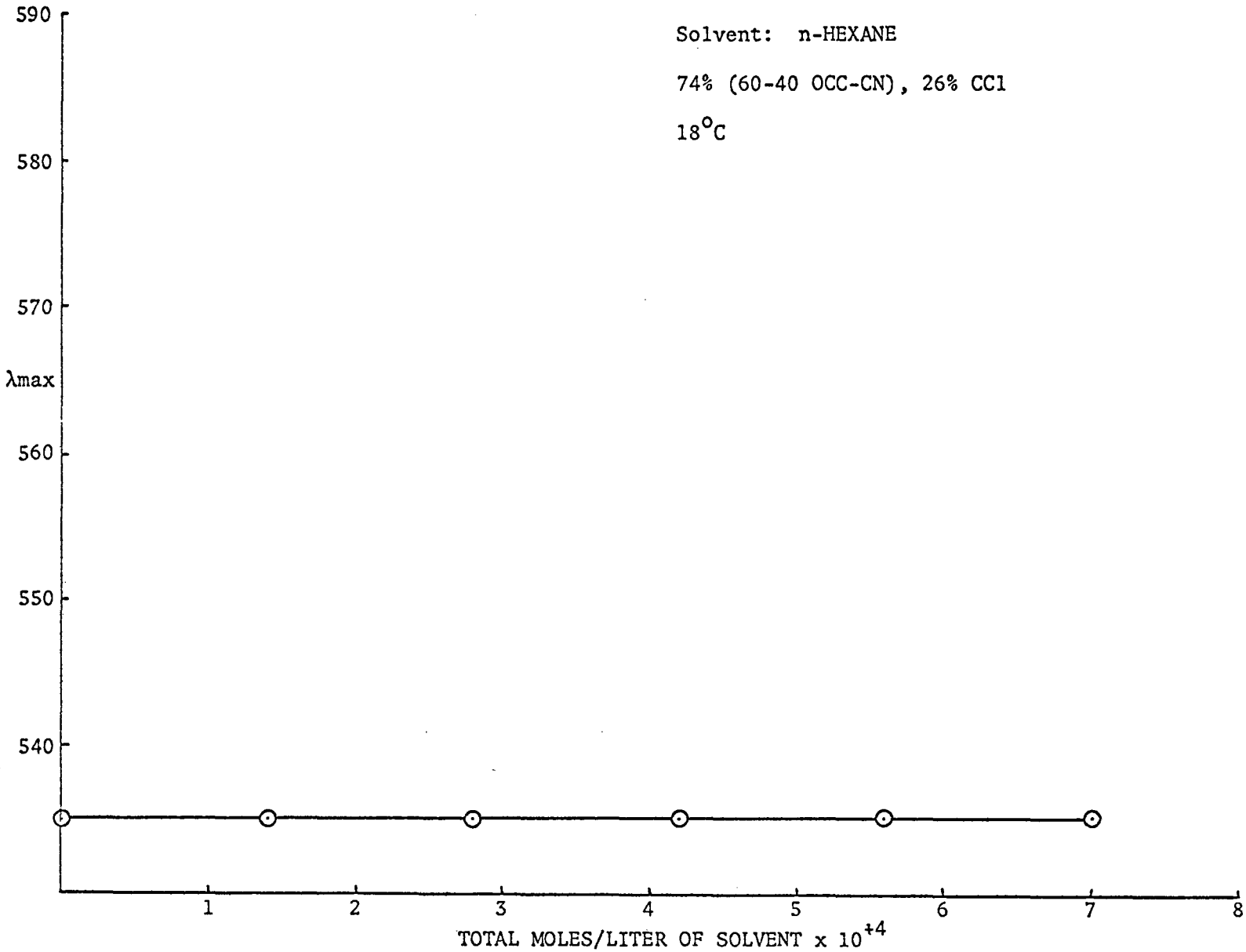


FIGURE 60

Solvent: CYCLOHEXANE

74% (60-40 OCC-CN), 26% CCl

18°C

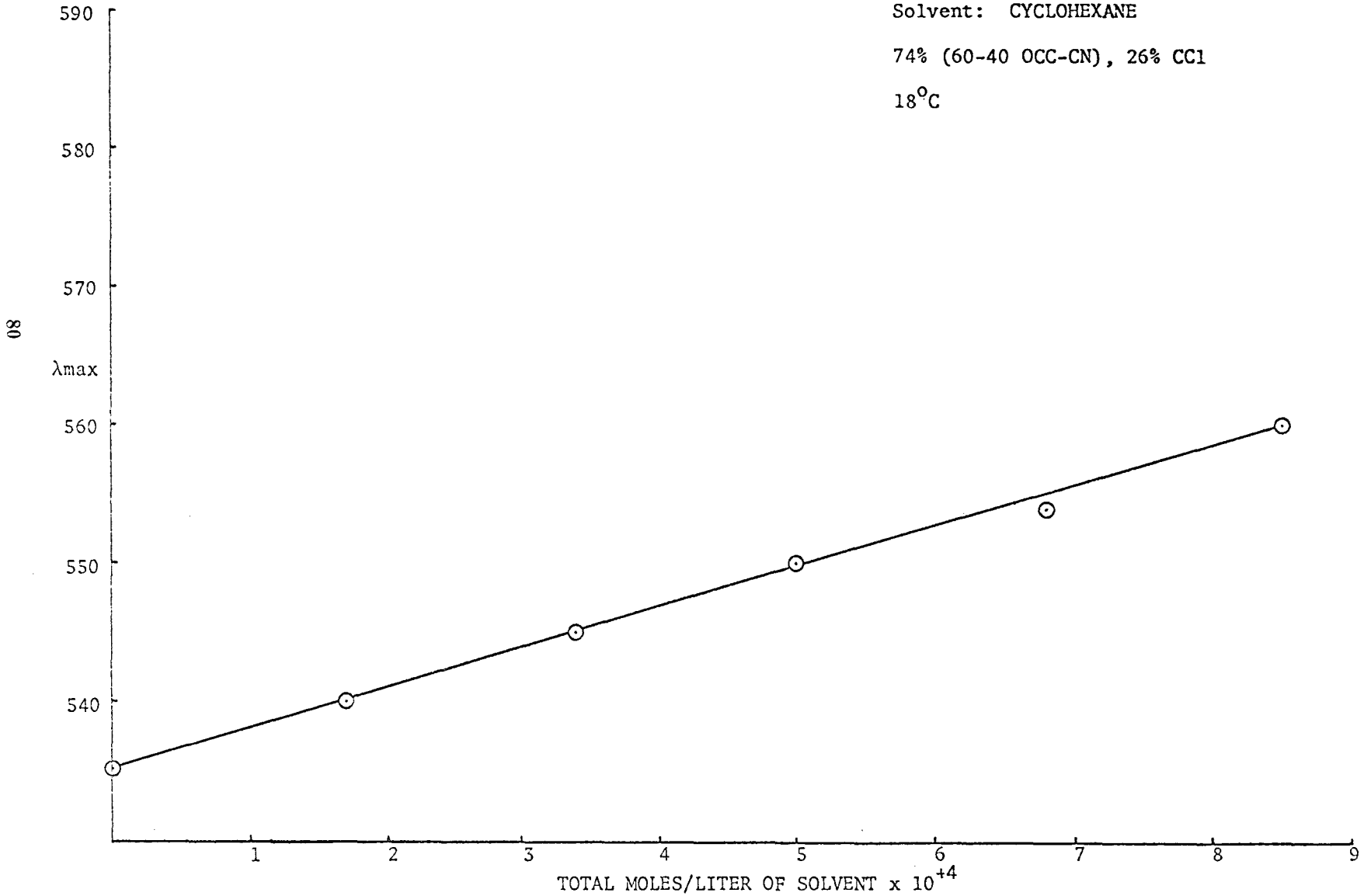


FIGURE 61

Solvent:n-NONANE

74% (60-40 OCC-CN), 26% CCl

18°C

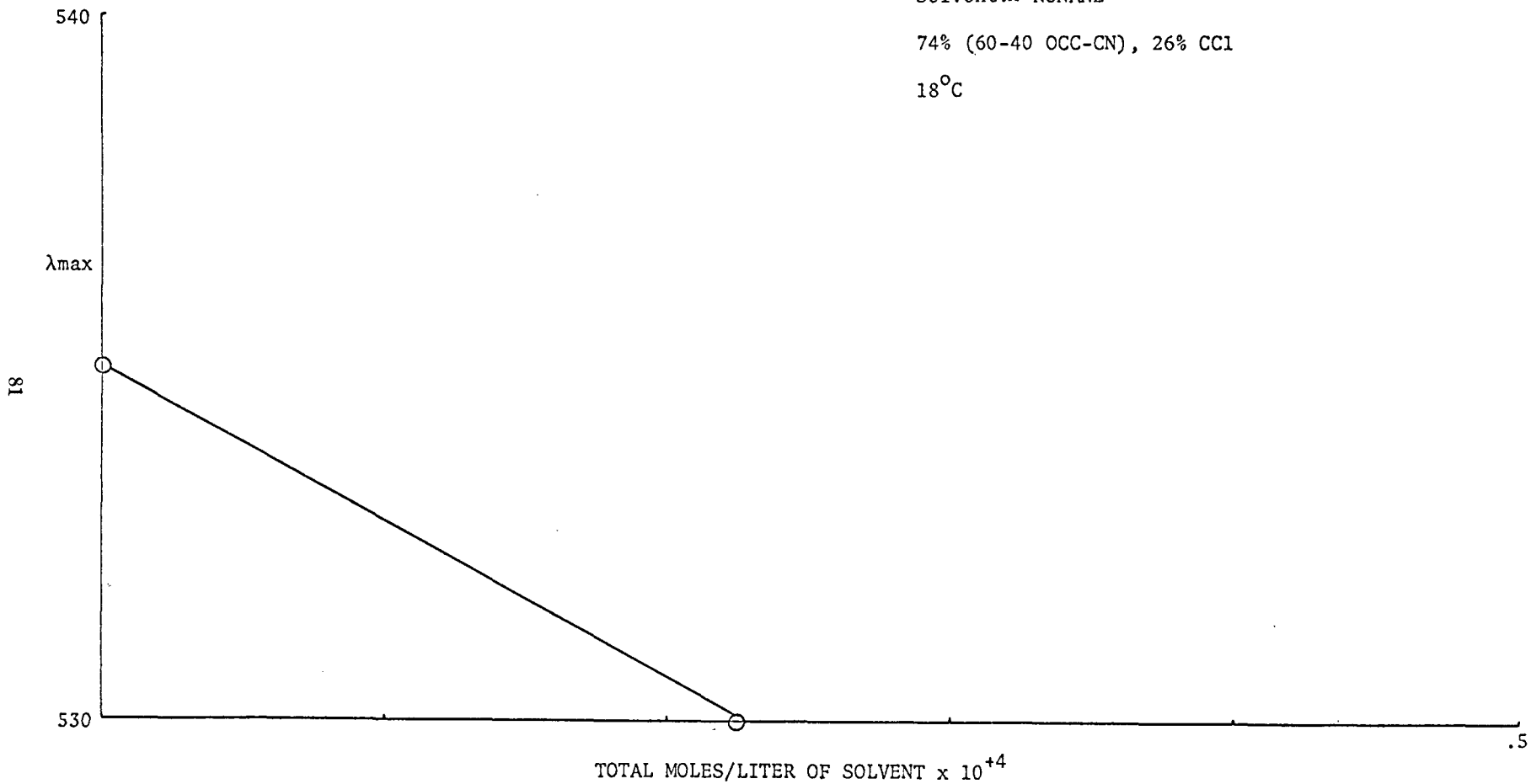


FIGURE 62

Solvent: ETHANOL

74% (60-40 OCC-CN), 26% CCl

18°C

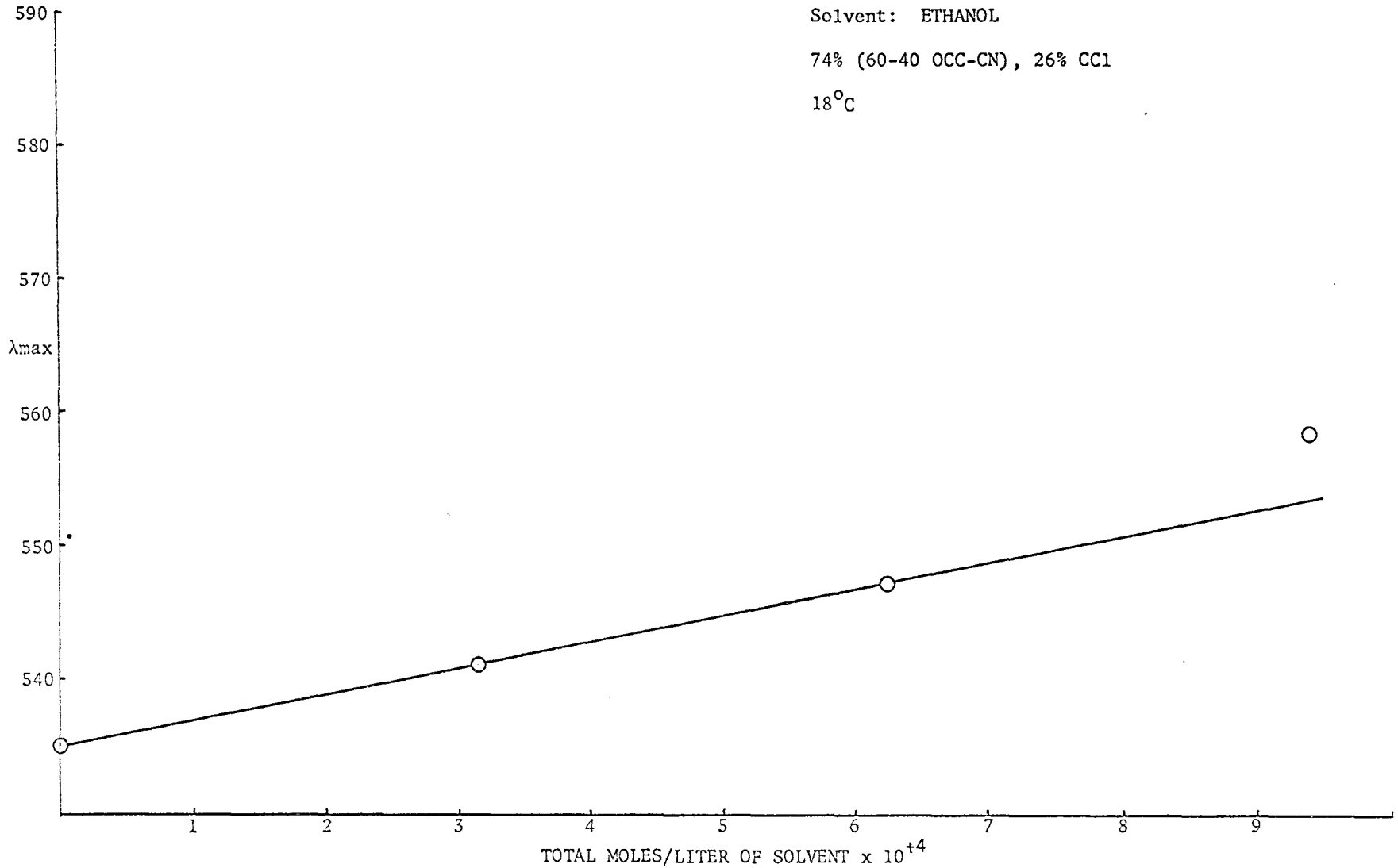


FIGURE 63

Solvent: ETHYL ACETATE

74% (60-40, OCC-CN), 26% CCl

18°C

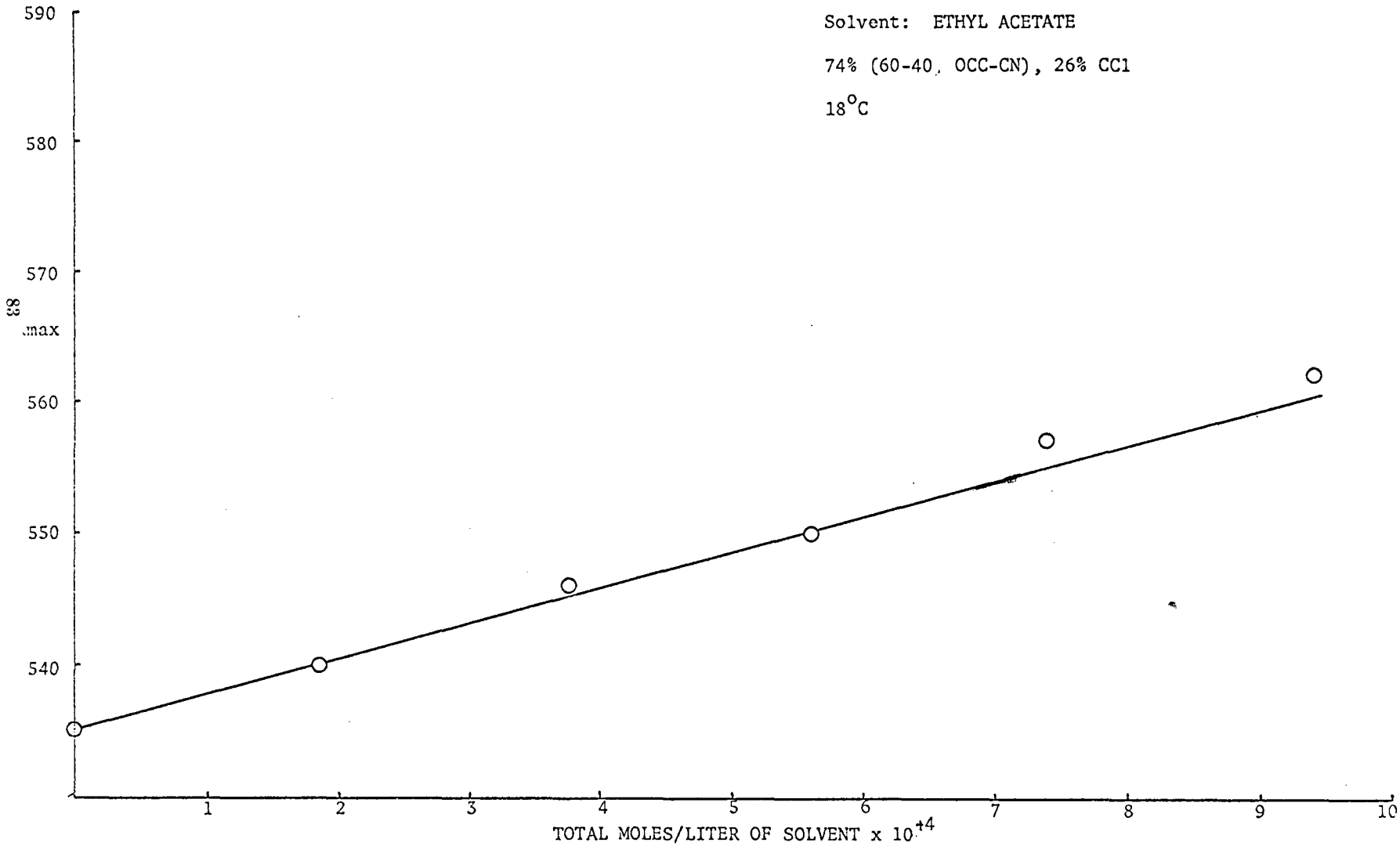


FIGURE 64

Solvent: DICHLOROMETHANE

72% (60-40 OCC-CN), 28% CCl

18°C

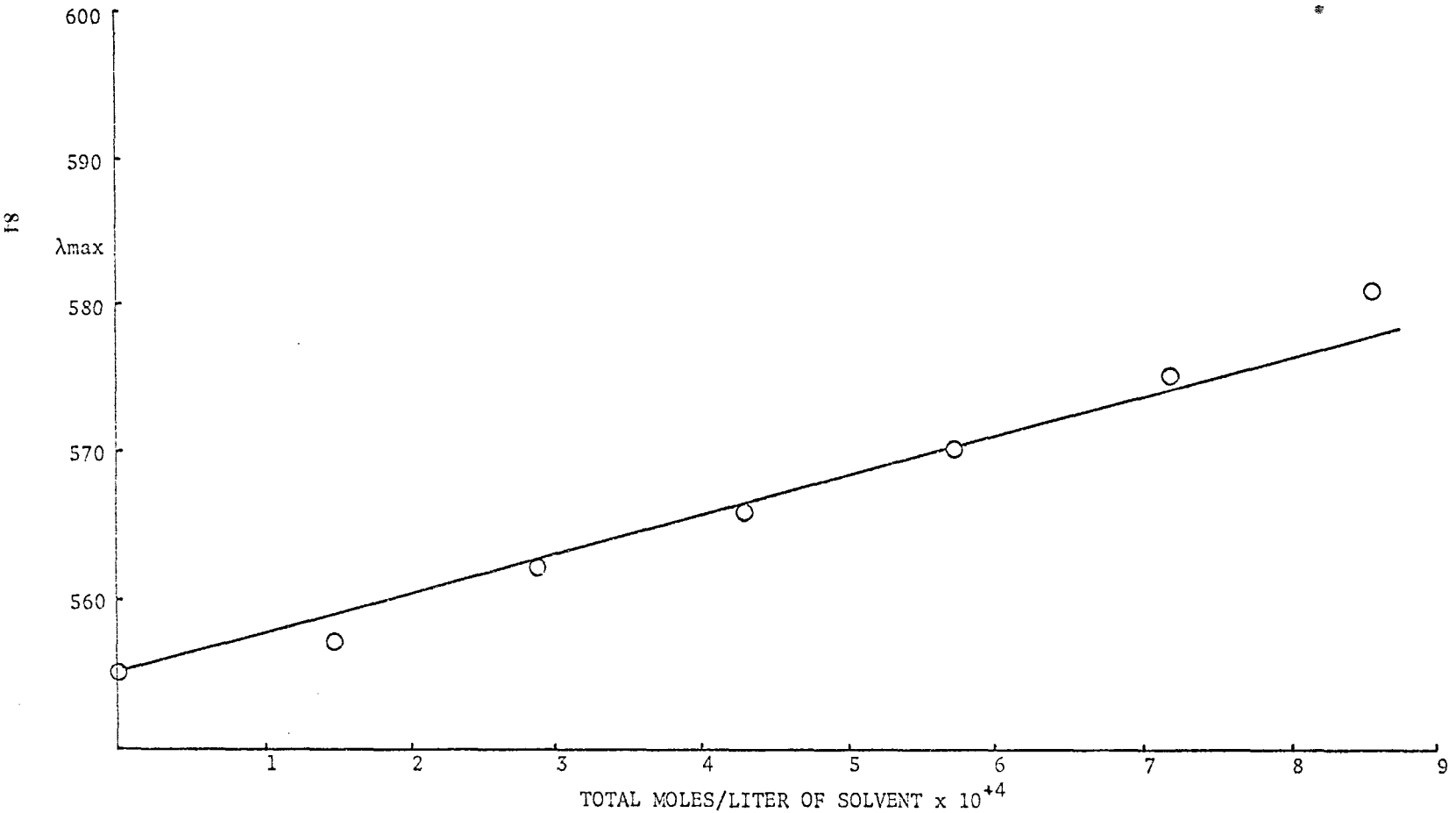


FIGURE 65

Solvent: CHLOROFORM

72% (60-40 OCC-CN), 28% CCl

18°C

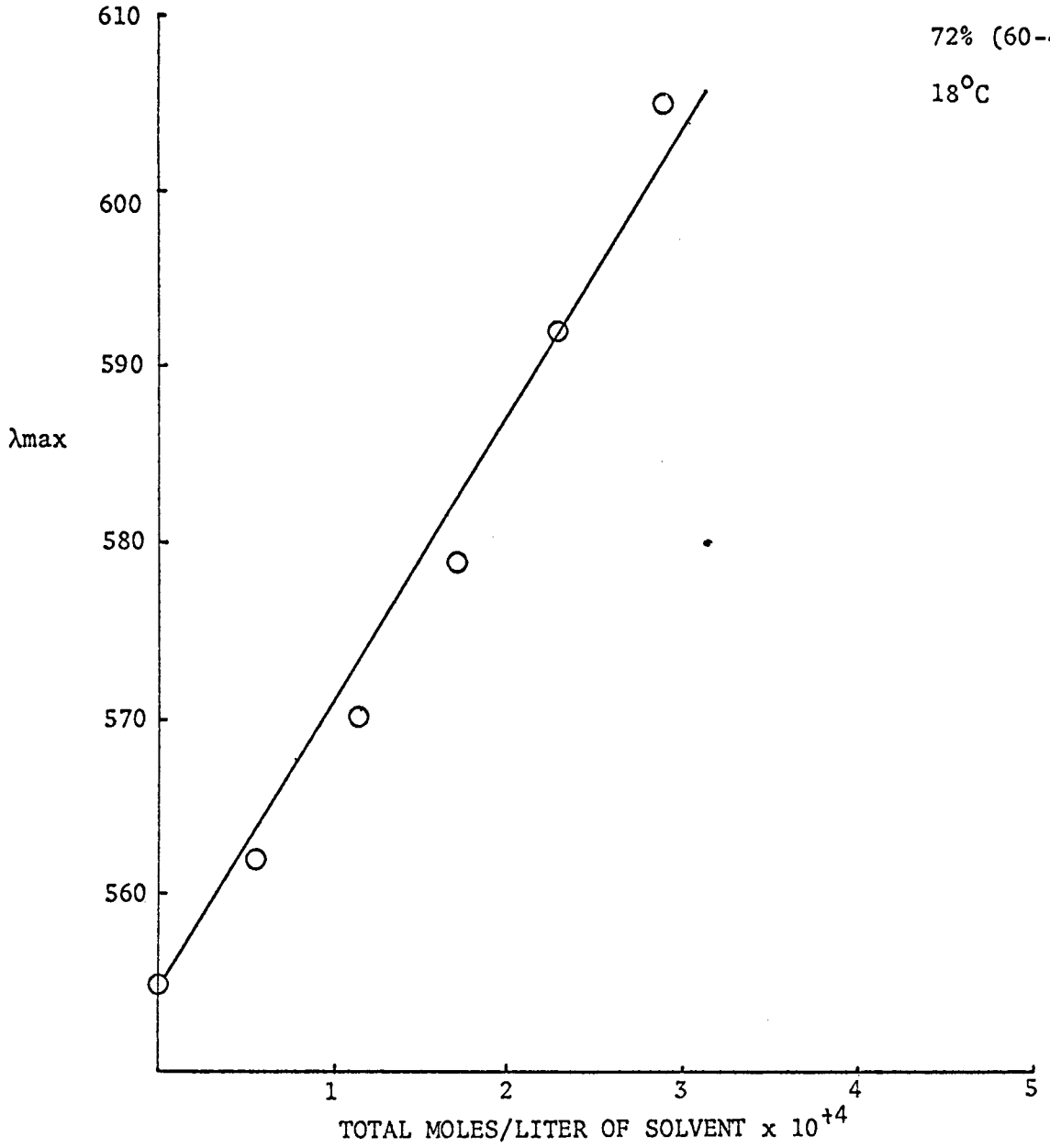


FIGURE 66

Solvent: CARBON TETRACHLORIDE

72% (60-40 OCC-CN), 28% CCl

18°C

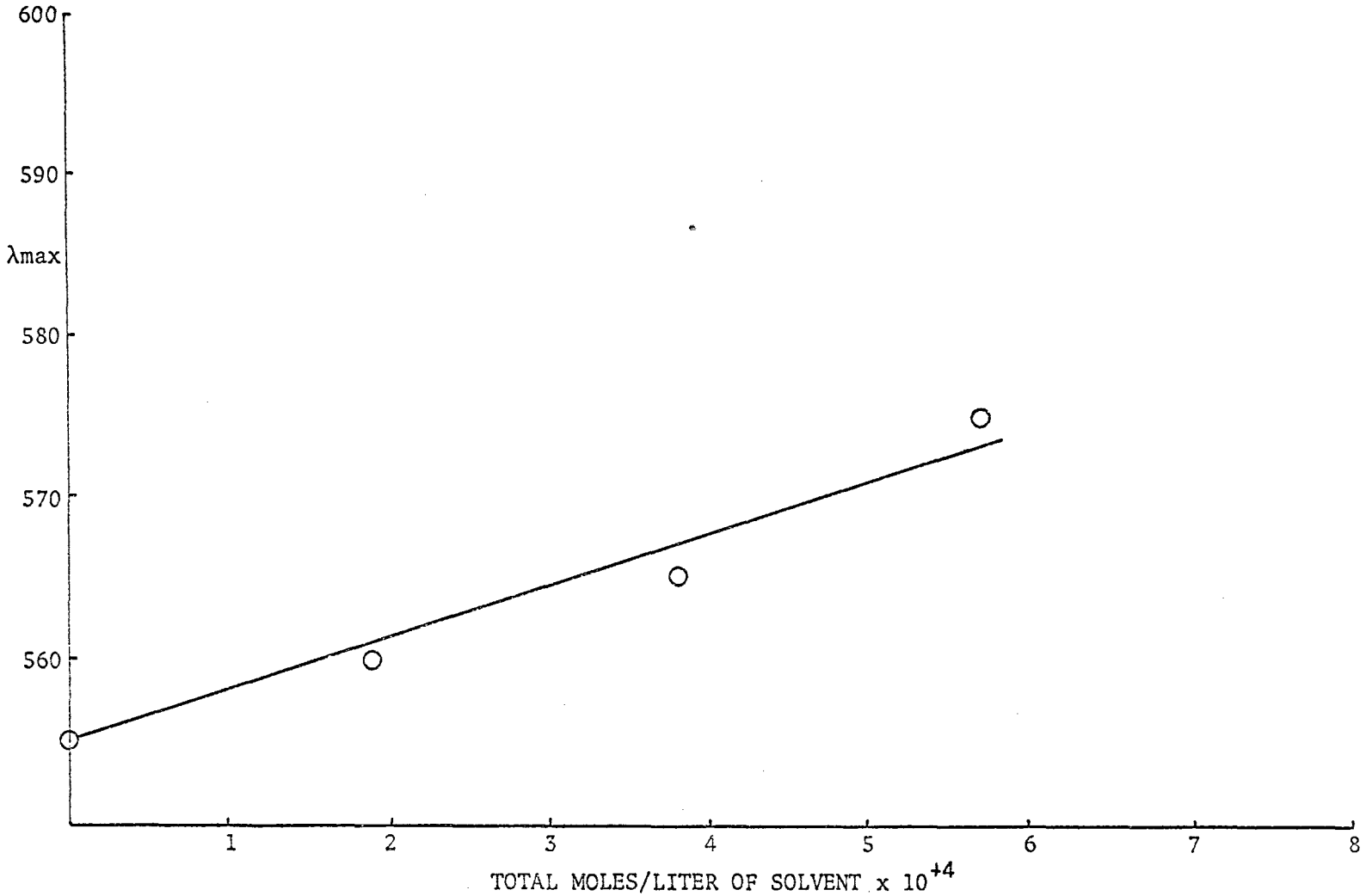


FIGURE 67

Solvent: BENZENE

72% (60-40 OCC-CN), 28% CCl

18°C

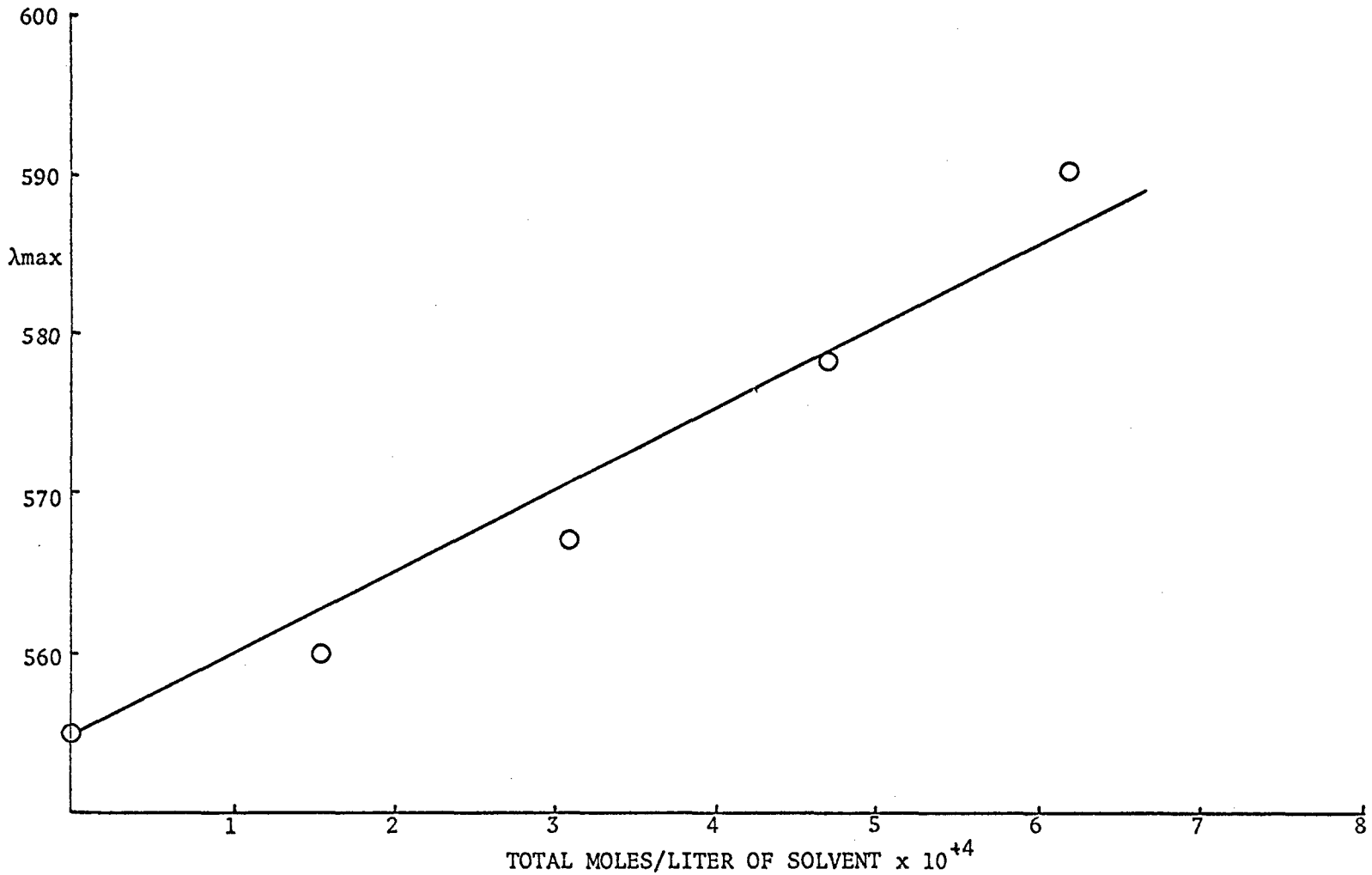


FIGURE 68

Solvent: o-XYLENE

72% (60-40 OCC-CN), 28% CCl

18°C

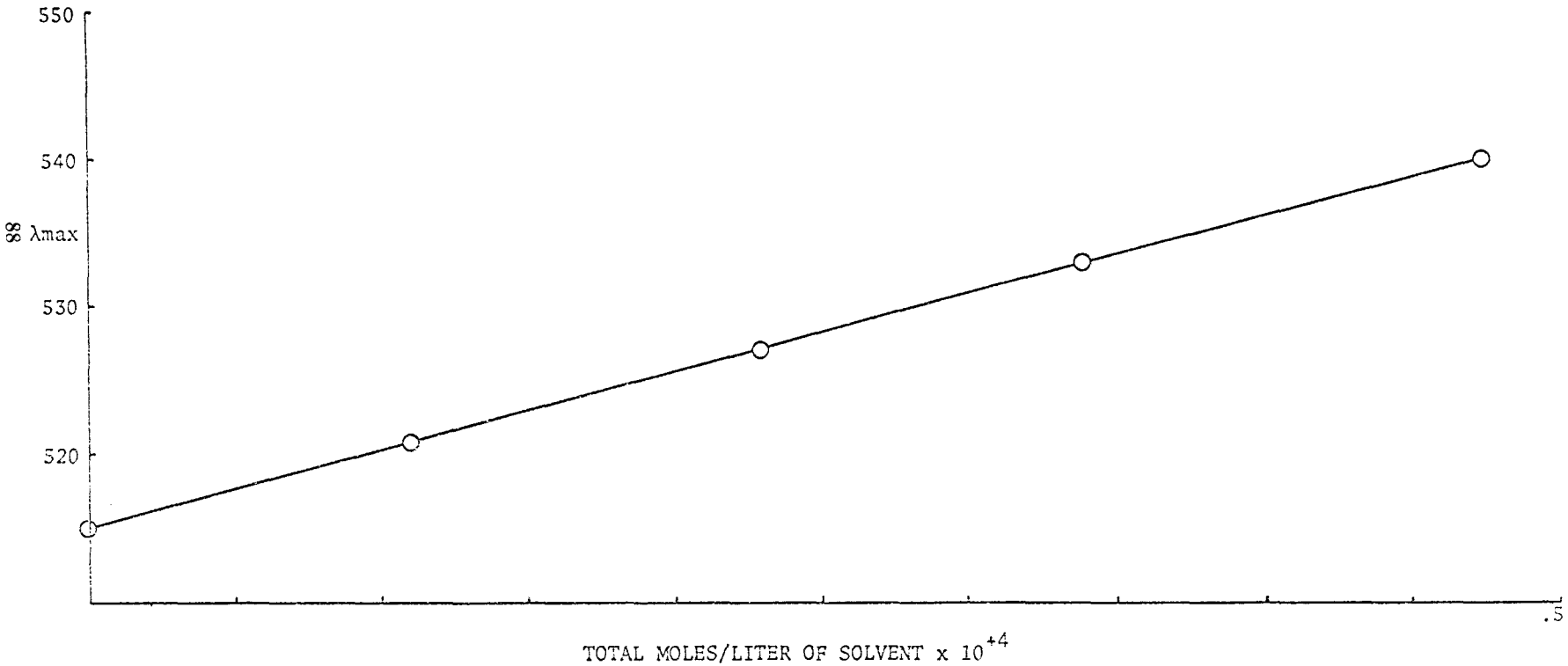


FIGURE 69

Solvent: m-XYLENE

72% (60-40 OCC-CN), 28% CCl

18°C

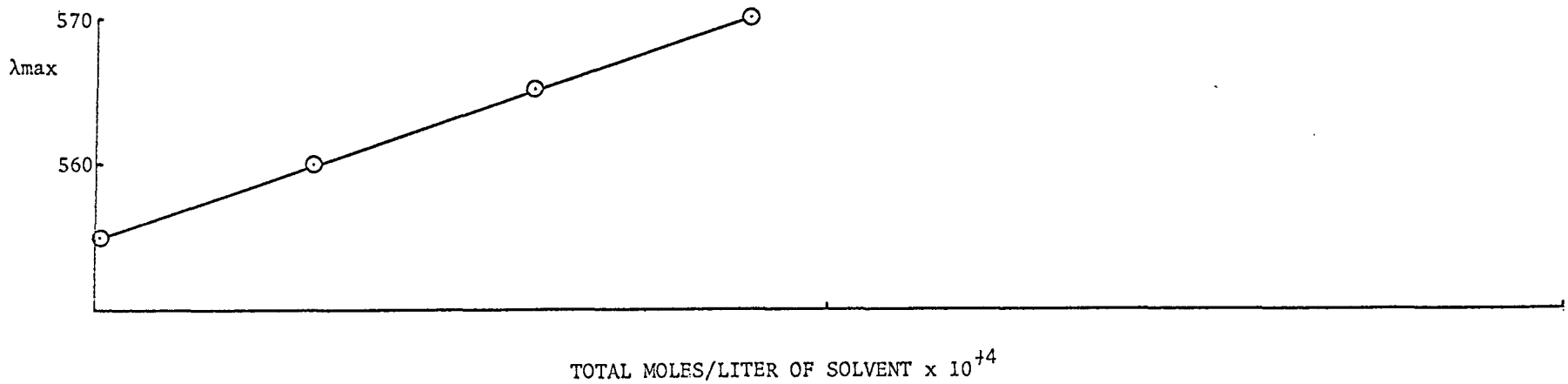


FIGURE 70

Solvent: p-XYLENE

72% (60-40 OCC-CN), 28% CCl

18°C

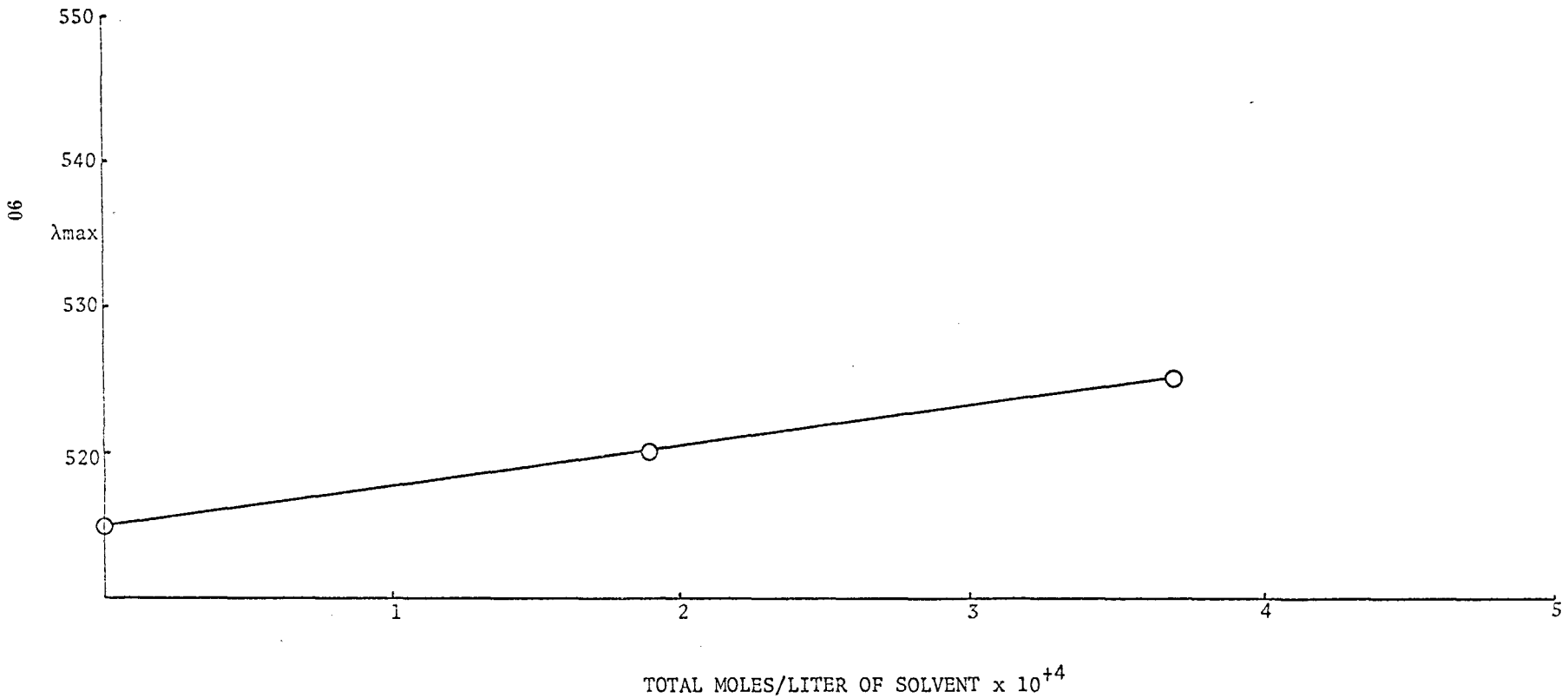


FIGURE 71

Solvent: n-HEXANE

72% (60-40 OCC-CN), 28% CCl

18°C

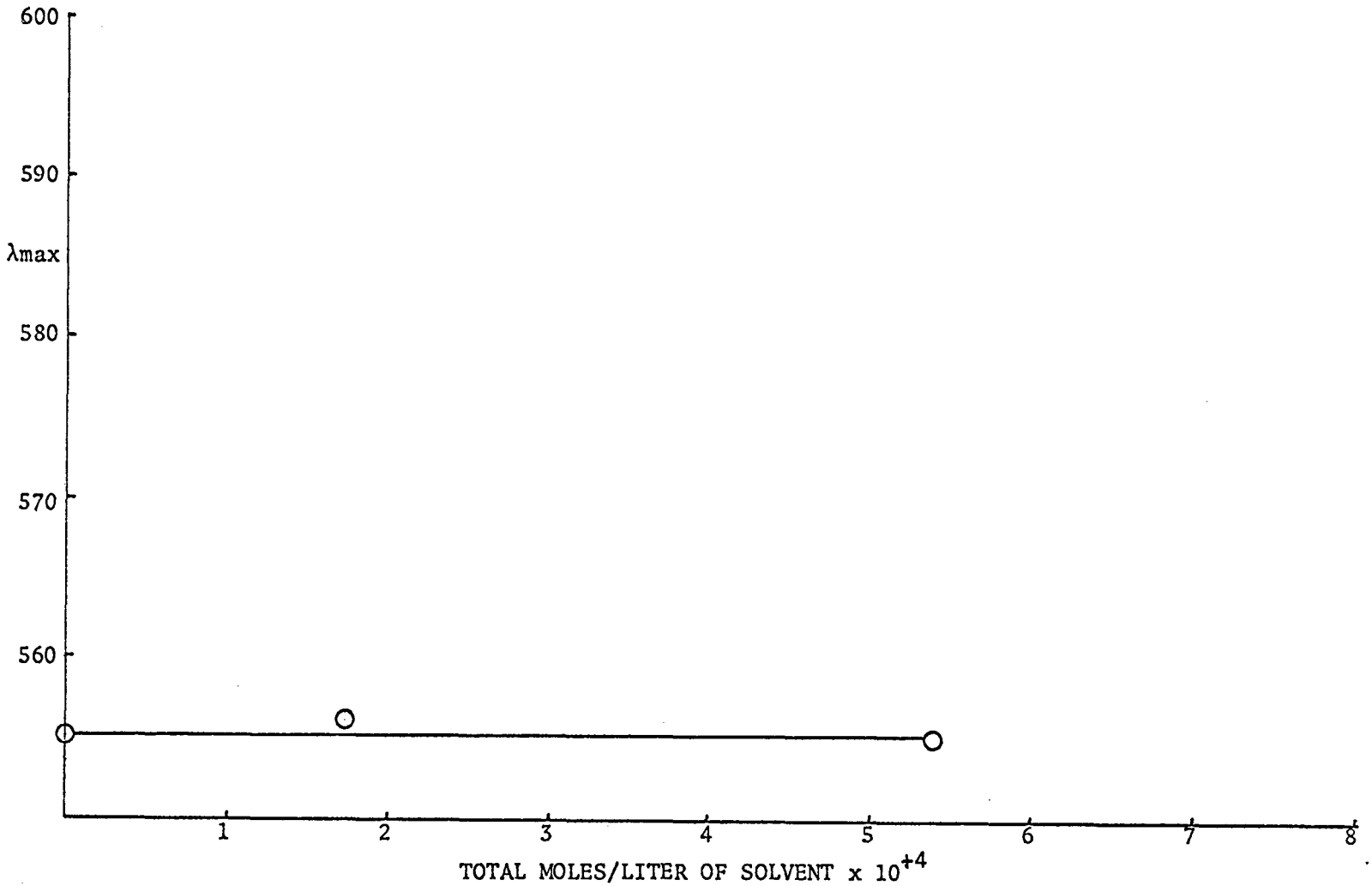


FIGURE 72

Solvent: CYCLOHEXANE

72% (60-40 OCC-CN), 28% CCl

18°C

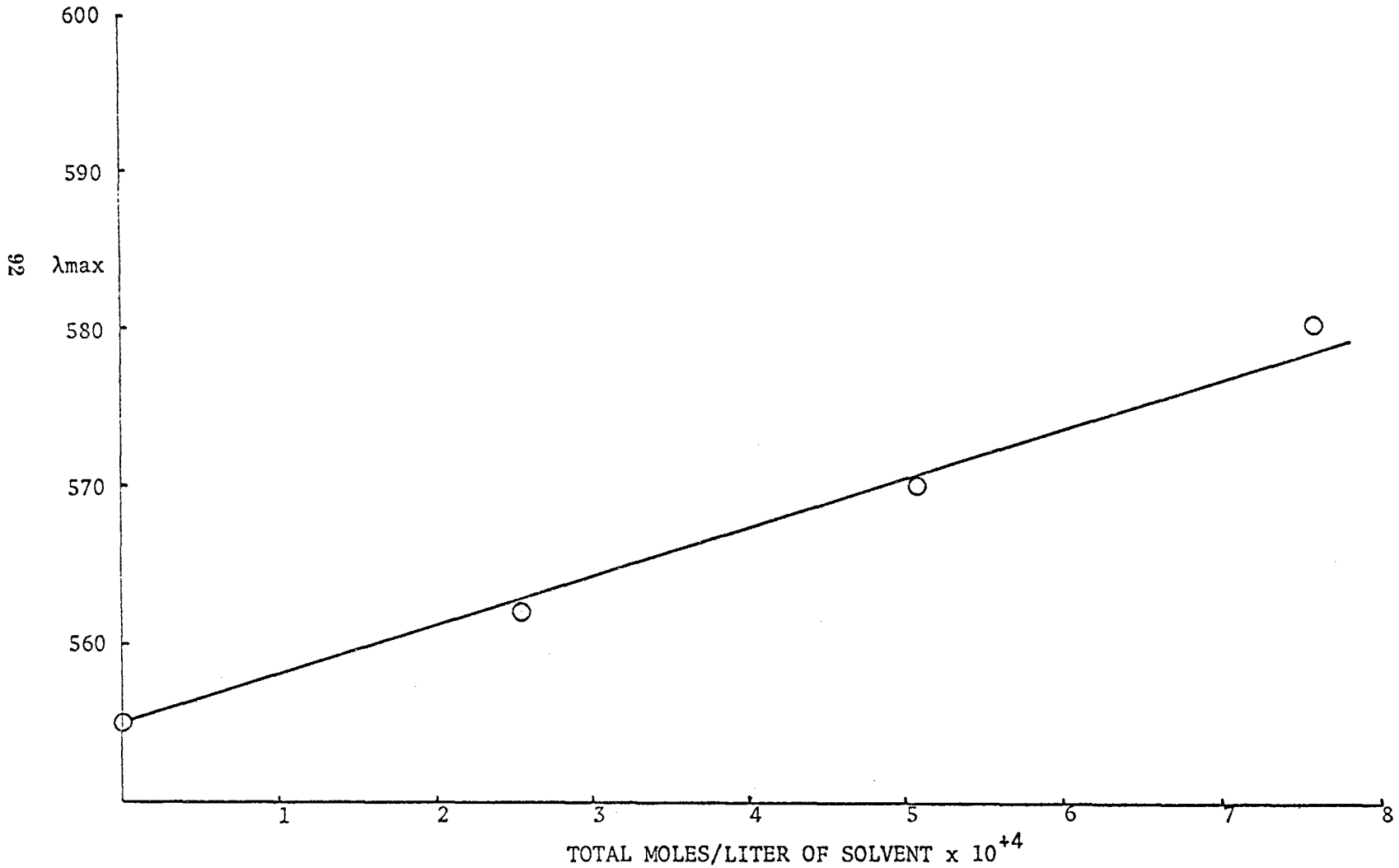


FIGURE 73

Solvent: n-NONANE

72% (60-40 OCC-CN), 28% CCl

18°C

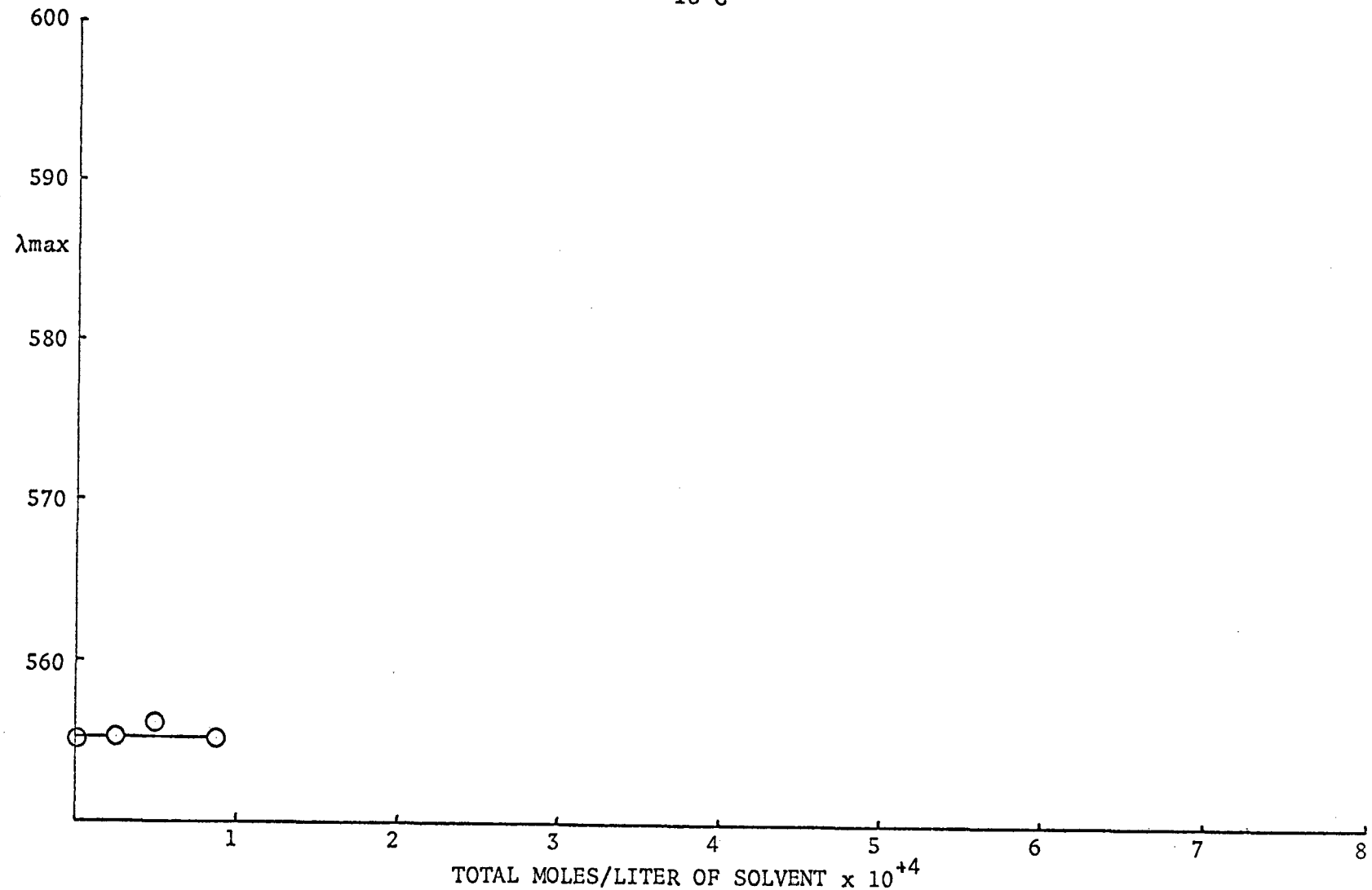
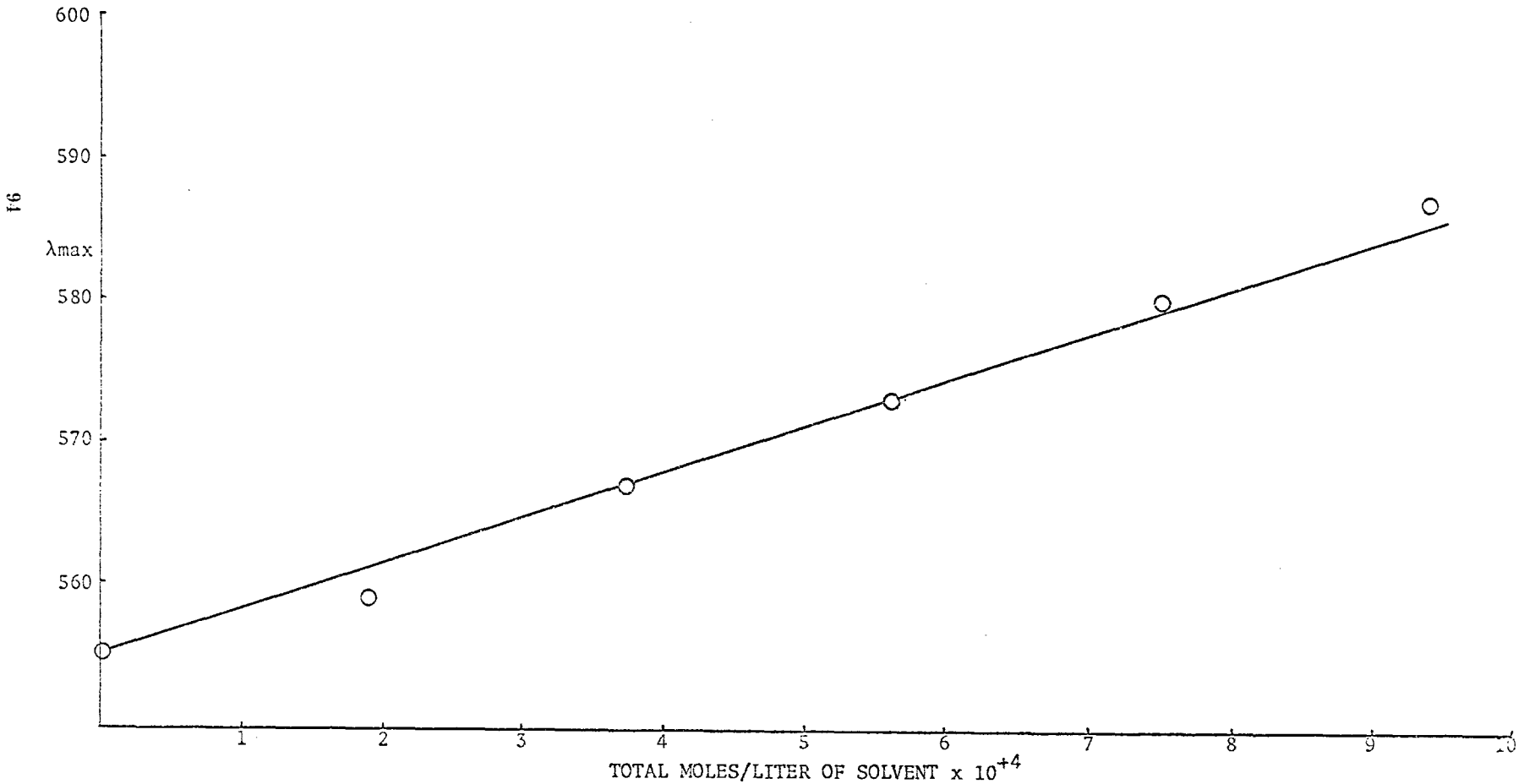


FIGURE 74

Solvent: ETHYL ACETATE

72% (60-40 OCC-CN), 28% CCl

18°C



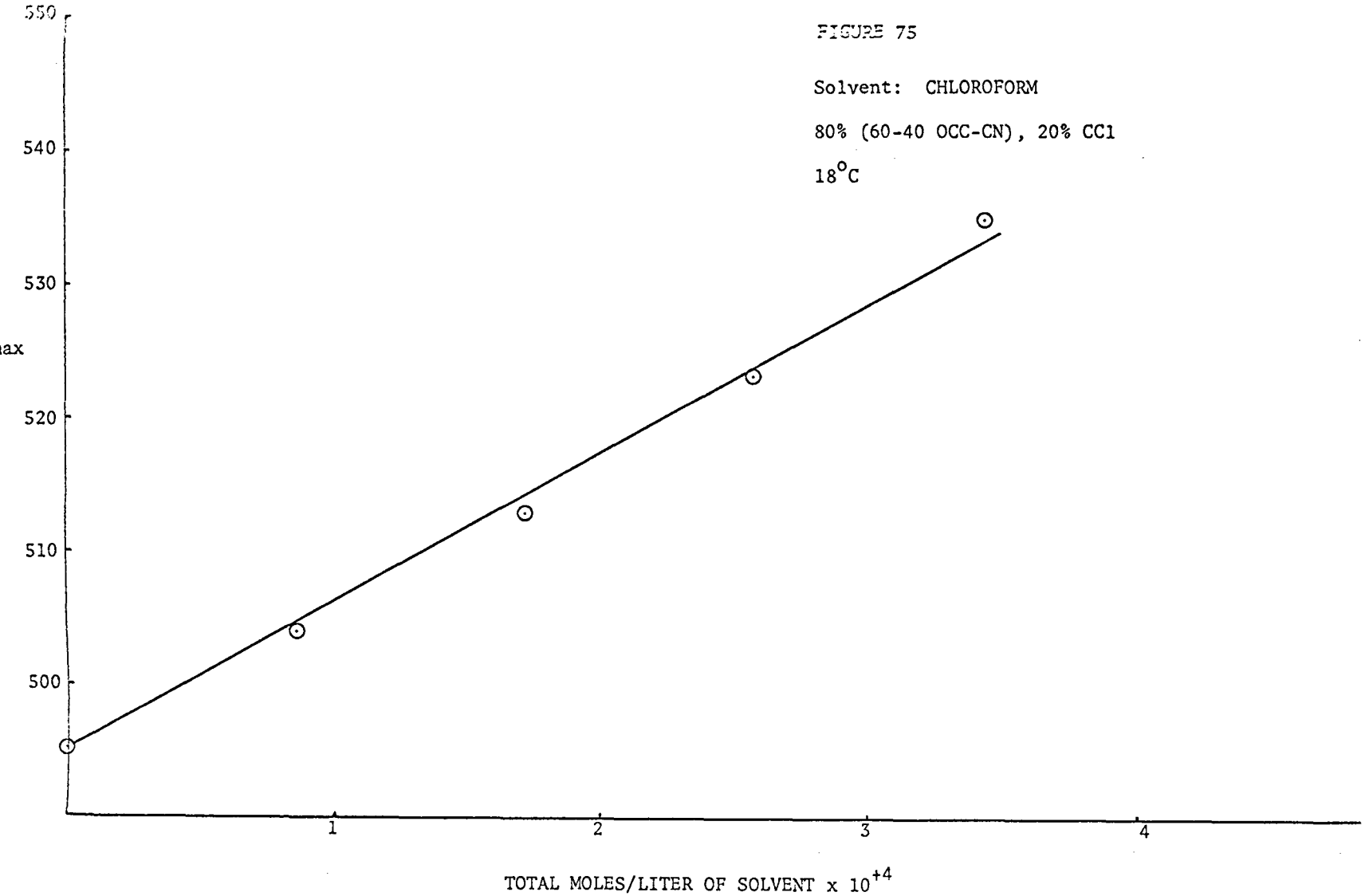


FIGURE 75

Solvent: CHLOROFORM

80% (60-40 OCC-CN), 20% CCl

18°C

FIGURE 76

Solvent: CARBON TETRACHLORIDE

80% (60-40 OCC-CN), 20% CCl

18°C

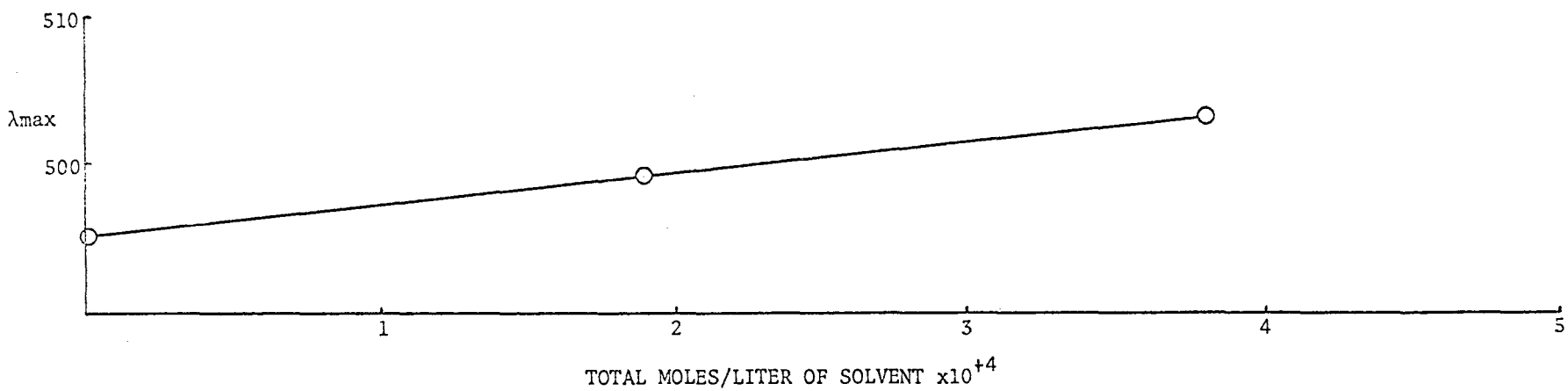


FIGURE 77

Solvent: DICHLOROMETHANE

80% (60-40 OCC-CN), 20% CCl

18°C

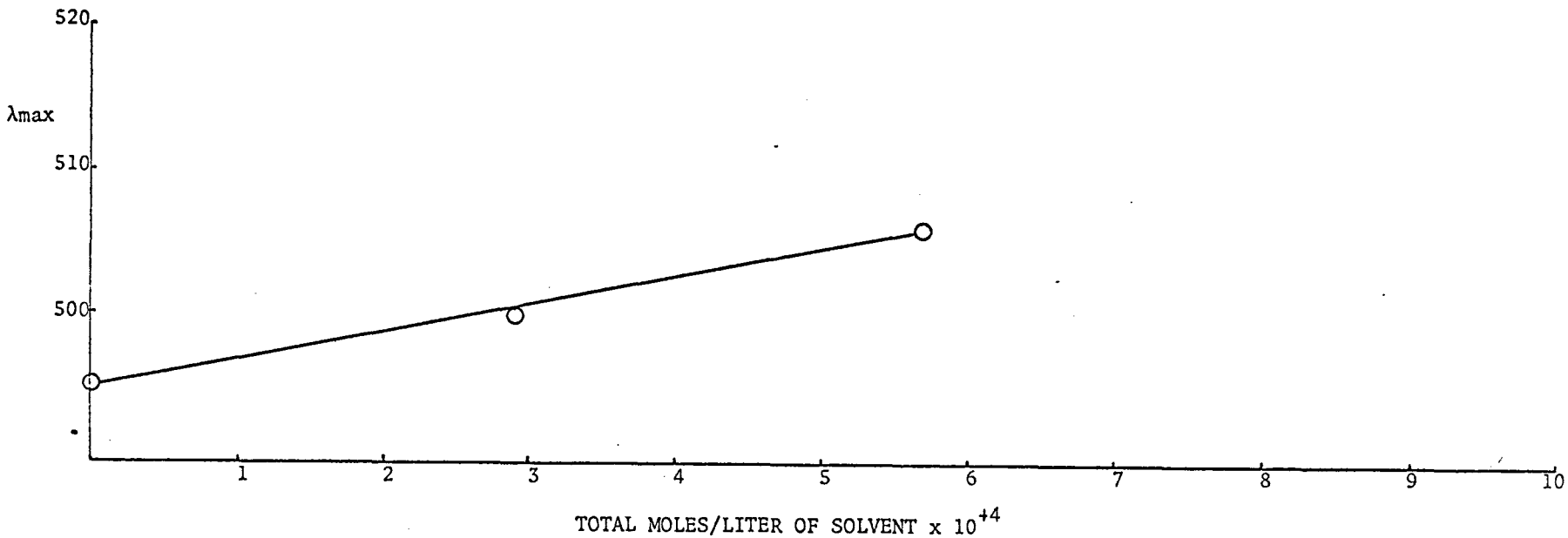


FIGURE 78

Solvent: BENZENE

80% (60-40 OCC-CN), 20% CCl

18°C

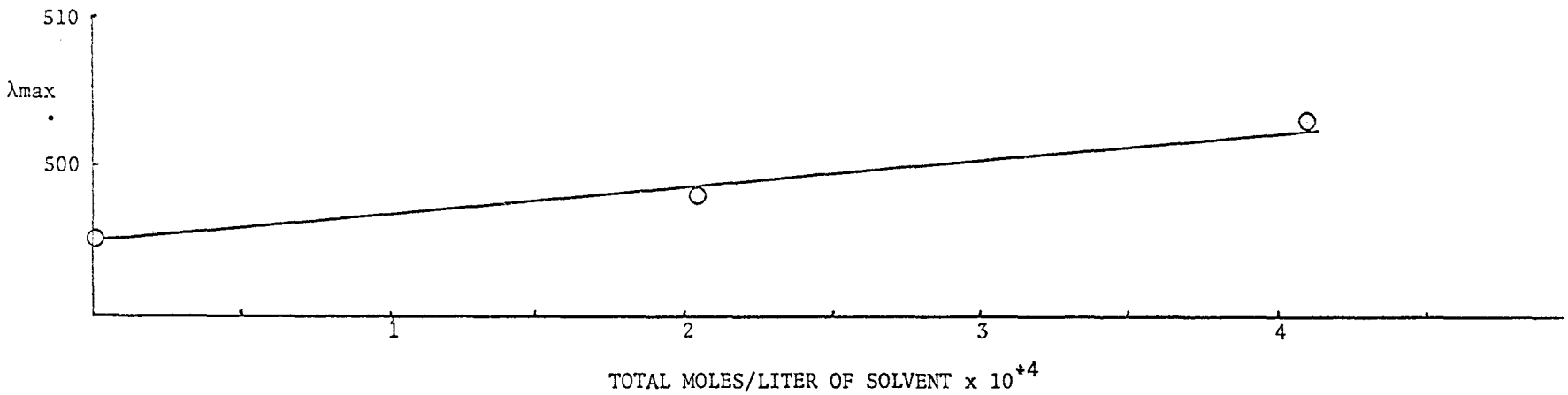


FIGURE 79

Solvent: n-HEXANE

80% (60-40 OCC-CN), 20% CCl

18°C

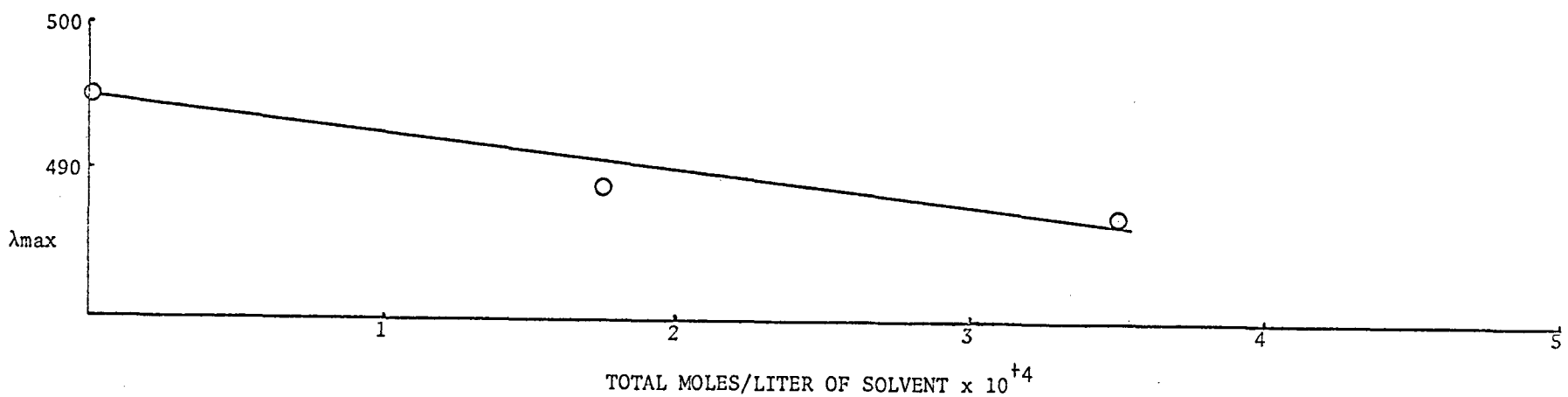


FIGURE 80

Solvent: n-NONANE

80% (60-40 OCC-CN), 20% CCl

18°C

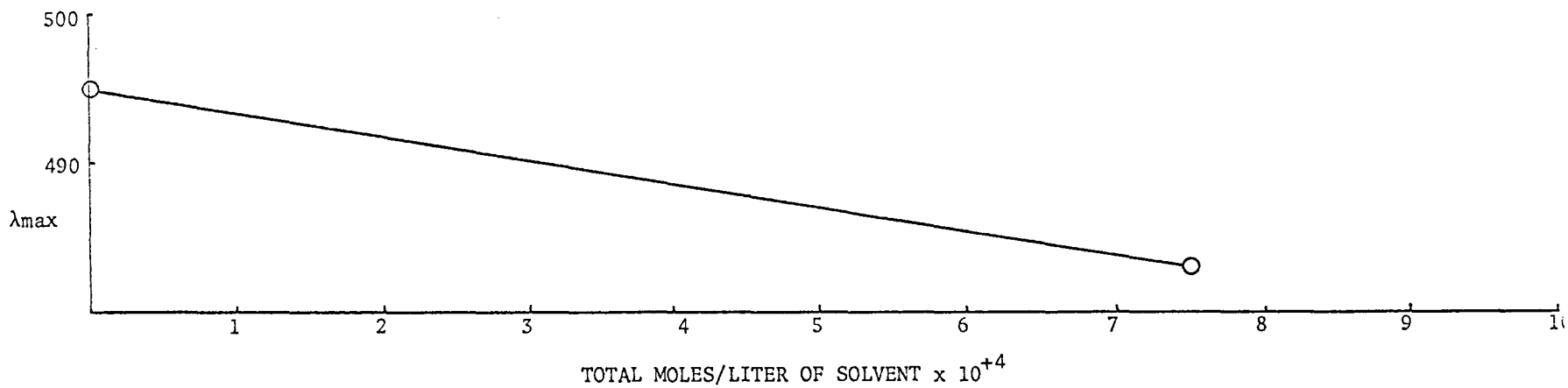
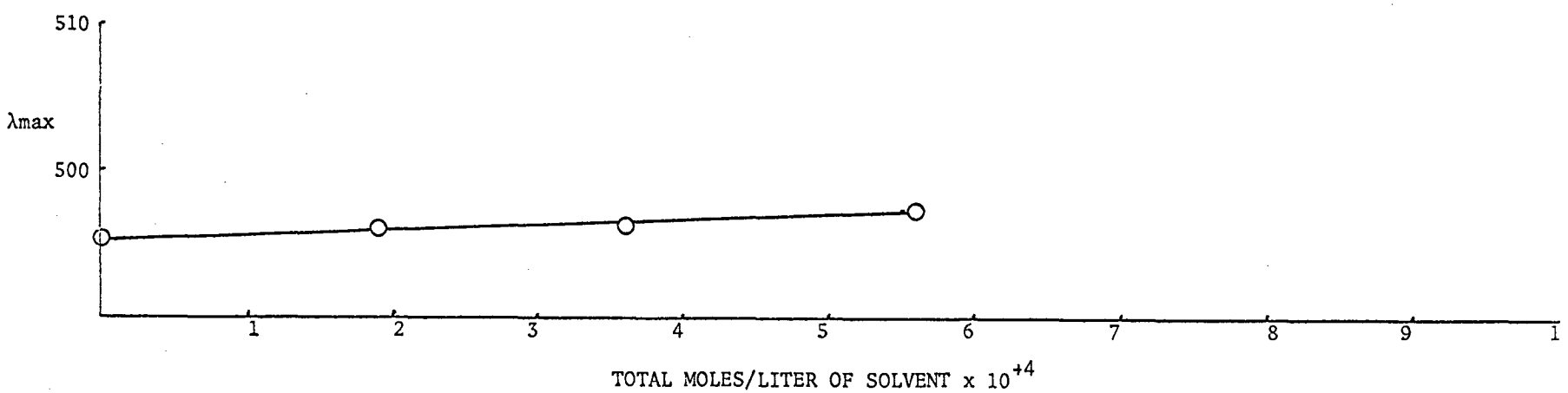


FIGURE 81

Solvent: ETHYL ACETATE

80% (60-40 OCC-CN), 20% CCl

18°C



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