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Relative Donor Properties of Various Propyl Ketones in Iodine Solution Using Spectroscopic Methods

by

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Submitted in partial fulfillment of the
requirements for the Senior Scholars Program

Colby College
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Abstract

Ketones in iodine solution are capable of transferring a nonbonding electron from the carbonyl oxygen to a halogen molecule forming a charge transfer complex. The electron-repelling nature of alkyl groups on either side of the carbonyl contributes to electron density and makes the ketone a better donor. The equilibrium constant of complex formation is an experimental measure of relative donor basicity and a theoretical measure of inductive effects. This study has determined that (1) the difference in inductive nature between a n-propyl and a methyl group is apparently negligible and (2) equilibrium constants may not be correlated with inductive effects when a substituent group interacts with the π-electrons of the carbonyl.

Introduction

The color of an iodine solution depends on the nature of the solvent. Solutions of iodine in carbon tetrachloride, chloroform, bromoform, and aliphatic hydrocarbons are violet while those in alcohols, ethers, carbonyl compounds, weak acids, esters, and nitrogen-containing compounds range from brown to orange and yellow. Lachman[1] (1903) proposed an iodine-solvent equilibrium interaction. Noting that a brown solution became violet upon heating and returned to brown on cooling, he postulated that "addition products" of iodine are in equilibrium with the violet form of the halogen. Beckmann[2] (1909) decided that the dissolved iodine is in the diatomic state regardless of solution color.

Hildebrand and Glascock[3] (1909) presented the first quantitative evidence for the existence of coordination compounds. Measuring the molal freezing point lowering in violet and brown solutions, they found that ΔT_f's for the first group corresponded to results predicted by dilute solution laws while those for the second group were abnormally small. They postulated that "brown-solvent adducts" are formed. Finding the ratio of free to solvated iodine by light transmission through solutions of known concentration, they calculated the formation constant K for some oxygen-containing compounds with iodine in carbon tetrachloride.

Weiss[4] (1942) attributed stability of such molecular adducts to the formation of ion pairs, D^+A^-. He recognized that low ionization potential of the donor molecule and high electron affinity of the acceptor molecule favor a stable complex and that its color in solution may be attributed to intense charge resonance spectra arising within the ions of the complex. Brackmann[5] (1949) attributed molecular complex formation to "complex resonance," quantum mechanical resonance between a no-bond and a bonding structure. The two components interact so strongly that physical properties of the solution must be attributed to the complex rather than either component alone, hence the solution's brown color. He realized that the reversible formation of resonance complexes might be the first step in some irreversible reactions.

Of the earlier work, the two most important were spectroscopic studies by Benesi and Hildebrand[6], and Mulliken.[7,8] Benesi and Hildebrand (1949) analyzed ultraviolet and visible spectra of aromatic and other compounds in iodine solution and proposed acid-base action in complex formation. All solutions studied showed a peak attributable to iodine in the visible wavelength range (ca. 500 mμ); aromatic solutions produced in addition an ultraviolet peak (ca. 300 mμ) or charge transfer (CT) band due to complex absorption. This is not, as Mulliken originally suggested, a modified aromatic band. With increased alkylation of the benzene core (e.g. the series benzene, toluene, o-, p-xylene, mesitylene) the CT band shifts to shorter wavelengths (farther to the ultraviolet) and more stable complexes with larger $\underline{K}$'s are formed.

Mulliken contributed the quantum mechanical wave analysis of charge transfer. He suggested a ground state wave function ψ_N with more covalent than ionic character and an excited state wave function ψ_E whose ionic character is much greater than covalent. Charge transfer occurs between molecular orbitals centered on different atoms which may or may not be in the same molecule. An intense absorption band corresponds to the electronic transition $\psi_N \rightarrow \psi_E$.

One may define a Lewis base as any species with an electron pair which may be shared and a Lewis acid as any species which can bond to such a pair.[9] Andrews and Keefer[10] conveniently classify the neutral molecule Lewis bases and corresponding acids characteristic of charge transfer systems as follows: π-donors donate an electron from a bonding molecular orbital, *i.e.* from a carbon-carbon double bond in an unsaturated hydrocarbon, an aromatic compound, or a multiple bond system. These donors form relatively weak π-complexes with π-acceptors. Members of the second major group of Lewis bases are called n-donors. In these bases the donated electron comes from a non-bonding molecular orbital which in the free base is a lone pair. These include oxygen-containing compounds (*e.g.* alcohols, ethers, carbonyl compounds), nitrogen-containing compounds (*e.g.* aliphatic amines, pyridine), and the sulfur and selenium analogs of ethers. This type of donor combines with v-acceptors (vacant-orbital acceptors, *e.g.* BX_3, AlX_3, SnX_4) to form fairly stable compounds. Halogen molecules form adducts with both π- and n-donors.

Iodine is the most effective Lewis acid of the elemental halogens because it is the least electronegative, and the most easily polarizable, and therefore forms the most stable complexes. It is convenient to use because its addition products are soluble in carbon tetrachloride. For thermodynamic work this means that heats of formation will be free from contributions by large heats of solvation encountered in polar solvents and lattice energies encountered in solids.[11]

One must remember that in "molecular complexes" forces of coordination are feeble and in most cases the halogen-halogen bond remains intact. Most heats of complex formation are less than 10 kcal/mole. Complexes are usually sufficiently unstable that one must study the solution with which its components are in equilibrium rather than the complex directly. Visible spectrophotometric methods measure the change in the iodine molecule when charge transfer occurs; ultraviolet methods measure the charge-transfer transition itself; infrared methods measure the weakening of bonds (decrease in frequency) within the donor or acceptor.

The $\pi^* \longrightarrow \sigma^*$ transition in a molecular complex between an n-donor (e.g. a ketone) and a halogen molecule (e.g. iodine) requires a bit more energy than the corresponding transition in the free halogen. Thus the visible iodine peak usually seen at 520mμ is "blue-shifted" to shorter wavelengths and is seen between 460 and 480 mμ depending on the donor stength of the ketone. At all wavelengths along the peak, absorbance is directly related to the concentration of the complex wherever the Beer-Lambert law holds,

$$A_c = \varepsilon_c C_c \quad b$$

A_c, ε_c, and C_c are the absorbance, molar absorptivity, and concentration of the complex, respectively, at equilibrium, and b is the path length of the absorbing system. Drago[12] has developed an expression relating the equilibrium constant of complex formation to spectrophotometric absorbance measurements. By determining equilibrium constants for a series of similar Lewis bases one may determine their relative donor strengths. This has been done for many carbonyl compounds.[11, 13-23] The purpose of the present study is (1) to determine the relative donor strengths of symmetrical propyl ketones and (2) to determine the relative inductive effects of n-propyl, i-propyl, and cyclopropyl groups.

Experimental

1. Materials

Analytical reagent carbon tetrachloride (Mallinckrodt) was refluxed at least one hour with potassium hydroxide and distilled through a three-foot heated column packed with glass helices. Since carbon tetrachloride was found to dissolve Lubriseal readily, all joints were sealed with Teflon tape. A middle fraction (b.p. = 76.5-76.7°) was taken in each distillation. The solvent was stored in a glass bottle fitted with a dispenser buret. Carbon tetrachloride's solvent properties prohibited use of neoprene stoppers and rubber tubing. High quality white rubber stoppers were used in the system and produced no detectable change in the solvent over short periods of time.

Analytical reagent iodine (Mallinckrodt) was resublimed by gently heating a beaker containing a mixture of 75% iodine and 25% potassium iodide.[11] Iodine vapor condensed on a cold roundbottomed flask above the beaker. Pure iodine crystals were scraped into a glass weighing bottle and stored in a des~~s~~iccator over activated alumina. Iodine in carbon tetrachloride solution was found to have a molar absorptivity of 908 l. mole^{-1}cm^{-1} in agreement with a reported value.[13, 22]

All ketones except acetone were refluxed with Drierite for at least one hour and distilled immediately before use. A sufficient number of foreruns was taken to ensure a narrow boiling range and prevent presence of water. Middle-boiling fractions were distilled through a Vigreux column into clean roundbottomed flasks, sealed with Teflon tape, and stored in a des~~s~~iccator with calcium chloride. Table I indicates the source and boiling range of each ketone. Spectranalized acetone was used without further purification and stored in its original container sealed by a rubber septum. Portions were withdrawn using a hypodermic needle.

TABLE I

Ketone	b.p.[24]	b.p. (exptl.)	Pressure (mm)	Source, Purity
Acetone	56.5	---	---	Fisher, spectro.
4-Heptanone	144	141.0	---	Eastman, practical
Diisopropyl ketone	123	122.0-122.2	758.0	Aldrich
Dicyclopropyl ketone	---	162.0-162.3	758.0	Aldrich
Methyl cyclopropyl ketone	---	110.8-111.8	---	Aldrich

2. Procedure

Charge transfer solutions were 0.0005M in iodine and approximately equal to or less than 1M in ketone. Charge transfer complexes are unstable due to formation of triiodide ion in concentrated base solution,[11] and absorbance tends to increase or decrease radically, depending on where readings are taken relative to the wavelength of maximum absorbance. Since absorbance changes with time even at low donor concentrations, readings were taken as soon as possible after ketone and iodine came in contact. All absorbance data were taken on a Beckman DU spectrophotometer with matched glass-stoppered 1 cm cells; readings are accurate to ±1%. The absorbance difference was measured between charge transfer solutions and iodine solutions of the same concentration. This makes the instrument direct reading for change in iodine absorbance resulting from charge transfer.

Stock iodine solutions (0.025M) were prepared by weighing 0.1586g iodine into a 25ml volumetric flask and diluting with carbon tetrachloride. Sample iodine solutions (0.0005M) were prepared by diluting 0.2ml stock solution to 10ml. For charge transfer solutions, an approximate volume of ketone was weighed into a 10ml volumetric and diluted almost to the line with pure carbon tetrachloride. An aliquot of stock iodine solution was added to the dilute solution, preventing contact with concentrated base. Carbon tetrachloride was then added to the mark. A fresh iodine solution was prepared for each set of charge transfer solutions since iodine concentration was found to change slightly with evaporation, and iodine absorbance with temperature.

3. Method of Calculation

Drago has studied extensively the equilibrium of donor-acceptor systems $D + I_2 \rightleftharpoons DI_2$ and has developed[12] an expression for the extent of complex formation K as a function of spectrophotometric data.

$$K^{-1} = \frac{A - A^{o}}{\varepsilon_c - \varepsilon_I} - C_D^{\,o} - C_I^{\,o} + \frac{C_D^{\,o}\, C_I^{\,o}}{A - A^{o}}\,(\varepsilon_c - \varepsilon_I)$$

where $(A - A^{o})$ is the experimentally measured absorbance; ε_c and ε_I are molar absorptivities of the complex and iodine; and $C_D^{\,o}$ and $C_I^{\,o}$ are initial concentrations of ketone and iodine, respectively. This equation may be used to analyze data only in regions of the spectrum where absorption is directly related to the concentration of the complex, i.e. in the charge transfer region (λ_{max} = 240 to 300mμ) and in the "blue shift" region (460 to 480mμ). All quantities in the equation are experimentally determinable except K and ε_c which are characteristic of the complex at equilibrium. Exact concentration of the iodine blank and sample solutions may be determined by the Beer-Lambert law,

$$A^{o} = \varepsilon_I\, C_I^{\,o}\, b$$

The value of ε_I may be found in tables and should be verified experimentally for the system. Exact concentration of the donor in sample solutions is calculated from the weight of donor dissolved in a known volume of carbon tetrachloride.

For a given donor concentration $(A - A^{o})$ is measured and the equation reduces to one of two variables, $(\varepsilon_c - \varepsilon_I)$ and K^{-1} or x and y. For each arbitrarily chosen value of x, a y may be calculated; x and y are then plotted in the cartesian plane as abscissa and ordinate respectively. Using a range of donor concentrations with corresponding absorbances, one may plot any number of lines which in theory all intersect in one point. The coordinates of this point indicate the equilibrium constant and molar absorptivity characteristic of the complex. Usually the lines intersect in the same vicinity but not in a single point. In this case the values of K are averaged and the error determined. If fewer than seven values are considered, a range is determined and multiplied by an appropriate constant[25] to produce an error representing 95% confidence. A sample calculation of all quantities is given for acetone in the Appendix.

Results

Ketone-iodine systems are sensitive to time and high donor concentration. Drago[11] and Bhaskar[23] report formation of triiodide ion in concentrated solutions over a period of time. Triiodide formation is characterized by absorption at 363mμ, and complex instability can be noted by color change. Some solutions initially pink or orange change to yellow; others fade completely. For each ketone an appropriate concentration range was chosen so that simultaneously the complexes remained stable and the system absorbed appreciably (i.e. $A - A^o$ was in the range 0.035 to 0.150).[26] Readings were taken as soon as possible after ketone and iodine came in contact.

Quite by accident it was discovered that the order in which one prepares CT solutions is of great importance. Pipetting stock iodine solution directly into a volumetric containing ketone produces a CT solution so concentrated in base that the complex is destroyed no matter how dilute the final solution is. Because this factor was not discovered until April 9, 1969, there was not enough time to thoroughly study the equilibrium constant of each ketone at different wavelengths. Experimental determinations have been limited to those at 520 and 550mμ. Spectrophotometric data is given in Table II and equilibrium constant data in Table III. Other reported values are also indicated in the table.

TABLE II

Spectrophotometric Data for Iodine Adducts in Carbon Tetrachloride

Donor	λ (mμ)	C_I^o (moles/liter)	A^o	C_D^o (moles/liter)	$A - A^o$
$CH_3C(O)CH_3$	550	0.0005	0.453	0.5045	0.075
				.7696	.100
				1.0315	.118
				1.3423	.134
$CH_3CH_2CH_2C(O)CH_2CH_2CH_3$	550	.0005	.453	.2793	.042
				.5697	.071
				.7107	.082
$(CH_3)_2CHC(O)CH(CH_3)_2$	520	.0005	.445	.3442	.041
				.6146	.066
				.9114	.089
				1.1686	.106
$C_3H_5C(O)C_3H_5$	550	.0005	.459	.3464	.071
				.5187	.090
				.7057	.102
				.8676	.112
$CH_3C(O)C_3H_5$	520	.0005	.470	.1004	.036
				.2096	.064
				.4259	.110
				.6182	.141

Though iodine adducts of diisopropyl ketone are soluble in carbon tetrachloride, the ketone itself is so insoluble that CT solutions of appreciable base concentration remain opaque for sometime after the ketone has been diluted with solvent. Solutions had to be prepared by first adding iodine to ketone and then diluting. Absorbance data are therefore questionable and little weight should be attached to the equilibrium constant.

TABLE III

Equilibrium Constant Data for Iodine Adducts in Carbon Tetrachloride

Donor	λ (mμ)	$\varepsilon_c - \varepsilon_I$ (l./mole-cm)	K_c (l./mole)	Solvent
$C_3H_5C(O)C_3H_5$	550	-366	1.88 ± .35	CCl_4
$CH_3C(O)C_3H_5$	520	-685	1.117 ± .16	CCl_4
$CH_3CH_2CH_2C(O)CH_2CH_2CH_3$	520	-429	0.870 ± .06	CCl_4
$CH_3C(O)CH_3$	550	-510	0.850 ± .10	CCl_4
$(CH_3)_2CHC(O)CH(CH_3)_2$	520	-629	0.463 ± .02	CCl_4

Other Published Data

Donor	λ (mμ)	$\varepsilon_c - \varepsilon_I$ (l./mole-cm)	K_c (l./mole)	Solvent
$CH_3C(O)CH_3$ [22]	550	-612	0.85 ± .1	CCl_4
$CH_3C(O)CH_3$ [23]	476	---	0.8	Cyclohexane
$(CH_3)_2CHC(O)CH(CH_3)_2$ [23]	488	---	0.8	Cyclohexane

Discussion

Taft has studied the relative inductive effects of substituted alkyl groups.[27, 28] Bhaskar finds the electron-releasing character of an alkyl group R reflected in the electron density increase of the carbonyl bond in ketones $CH_3C(O)R$ and $RC(O)R$. Increased electron density makes such ketones better Lewis bases in iodine solution. Combining this information with a summary of inductive effects found in Fieser and Fieser,[29] a more complete series may be devised. Assigning hydrogen inductive neutrality, those above it in the series are increasingly electron-repelling and those below are electron-attracting. The series are summarized in Table IV.

TABLE IV

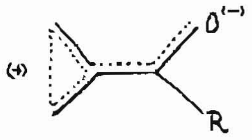
Relative Inductive Effects of Alkyl Substituents

Taft Series[29]	Bhaskar	Fieser and Fieser	Complete
t-butyl	t-butyl	t-butyl	t-butyl
ethyl	i-propyl	i-propyl	i-propyl
methyl	methyl	ethyl	n-propyl
hydrogen	ethyl	methyl	ethyl
benzyl	benzyl	hydrogen	methyl
		ethylene	hydrogen
		benzyl	cyclopropyl
			ethylene
			benzyl

Considering inductive effects only, the order of donor basicity for the ketones studied should be diisopropyl ketone > dipropyl ketone > acetone > methyl cyclopropyl ketone > dicyclopropyl ketone. (A cyclopropyl group should be intermediate between hydrogen and ethylene groups in "double-bond character" and ability to withdraw electrons.)

This series of donor basicity is not valid (see Table III) since there are other factors. Steric effects seem to be negligible since K for acetone and dipropyl ketone are essentially the same. Conjugative effects, however, appear to be important.

Kosower[30] has studied the carbonyl absorption of acetone, methyl cyclopropyl ketone, and dicyclopropyl ketone using water and isooctane as solvents. Molar absorptivities for the $n \rightarrow \pi^*$ carbonyl transition in isooctane are 1840; 5600; and 10,800 respectively. The intensity of electronic transition increases with substitution of cyclopropyl rings. In aqueous solution, the wavelength of maximum absorbance is found to shift toward visible. He concludes, "...comparison of the spectral data for the cyclopropyl ketones with that for acetone demonstrates that the cyclopropane ring must be contributing electronic charge to the carbonyl group. Delocalization may be indicated through such structures as



The present set of data appears to be the first which reports maxima with positions which must be ascribed to the interaction of a cyclopropyl ring with a π-electron system.*

This so-called π-interaction contributes significantly to the carbonyl's electron density and hence to the ketone's basicity. It greatly overshadows any electron-withdrawing inductive effect which occurs simultaneously. Two cyclopropyl rings appear to be even more effective than one at π-interaction, which explains the order dicyclopropyl ketone > methyl cyclopropyl ketone > acetone. However, π-interaction prohibits measure of a cyclopropyl group's relative electronattractive or -repelling nature.

In conclusion, it is suggested that in further study of how inductive effects affect donor basicity, only one substituent group be varied at a time. A series $CH_3C(O)R$ might have been more useful, where R = t-butyl, i-propyl, cyclopropyl, n-propyl, ethyl, methyl, hydrogen. This suggestion is made because of (1) the success in comparing dicyclopropyl to methyl cyclopropyl and to dimethyl ketone, and (2) the failure of comparing dipropyl to dimethyl ketone. Any increase in the carbonyl electron density created by an inductive effect is probably lost in the steric hindrance of two n-propyl groups flapping.

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Appendix I

Sample calculation of equilibrium constant and molar absorptivity for the acetone-iodine system in CCl_4.

(1) Initial Iodine Concentration

$$C_I^{\,o} = \frac{A^o}{\varepsilon_I b} = \frac{.453}{908 \text{ liters/mole}} = .0005 \text{ moles/liter}$$

(2) Initial Acetone Concentration

$$C_D^{\,o} = \frac{.2930 \text{ g}}{10 \text{ ml}} \times \frac{1 \text{ mole}}{58.08 \text{ g}} \simeq .5045 \text{ moles/liter}$$

(3) Spectrophotometric Data

(determined experimentally)

Solution	$C_D^{\,o}$	$A - A^o$
A	0.5045	-0.075
B	0.7696	-0.100
C	1.0315	-0.118
D	1.3423	-0.134

(4) Use Of Drago Equation for solution A

$$K^{-1} = \frac{A - A^o}{\varepsilon_c - \varepsilon_I} - C_D^{\,o} - C_I^{\,o} + \frac{C_D^{\,o}\, C_I^{\,o}}{A - A^o}\,(\varepsilon_c - \varepsilon_I)$$

$$Y = \frac{A - A^o}{X} - C_D^{\,o} - C_I^{\,o} + \frac{C_D^{\,o}\, C_I^{\,o}}{A - A^o}\, X$$

$$Y = -\frac{.075}{X} - .5050 + .003363\, X$$

(5) Equation is plotted by selecting values of x at random and calculating the corresponding value for y.

X	Y
-300	0.504
-500	1.117
-700	1.849

(6) Equations resulting from the other donor concentrations are plotted on the same axes.

B. $Y = -\frac{.100}{X} - .7701 + .003848X$

X	Y
-300	0.385
-500	1.154
-700	1.924

C. $Y = -\frac{.118}{X} - 1.0320 + .004371X$

-300	0.280
-500	1.154
-700	2.028

D. $Y = -\frac{.134}{X} - 1.3428 + .005008X$

-300	0.160
-500	1.162
-700	2.163

(7) The four lines intersect in the following manner

Intersection	$X = (\varepsilon_c - \varepsilon_I)$	$Y = K^{-1}$	$Y^{-1} = K$
CD	488	1.101	.990
BD	494	1.131	.884
BC	500	1.154	.867
AD	510	1.230	.813
AC	523	1.254	.797
AB	548	1.338	.747
	Avg. 510		Avg. .850

(8) Error calculation

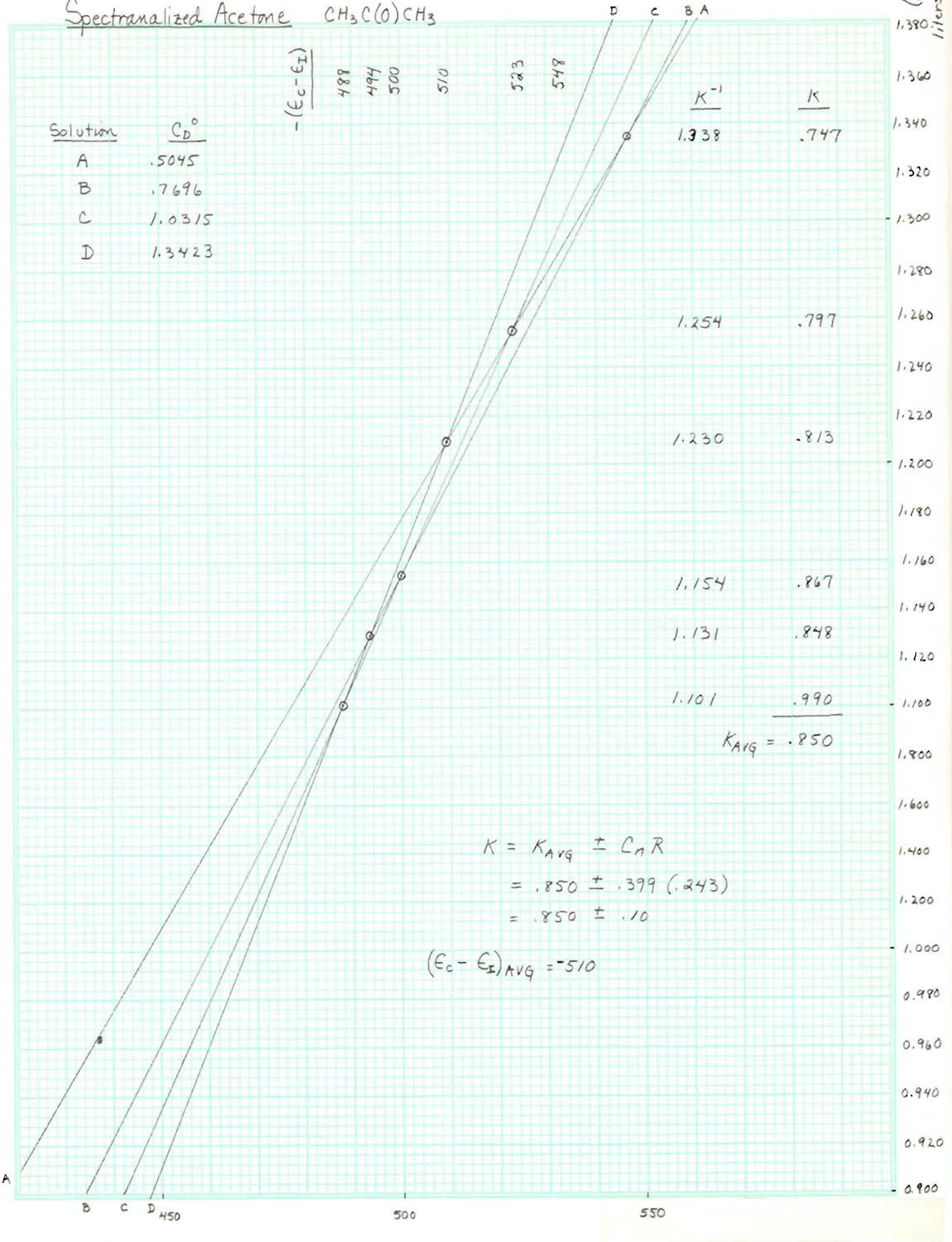
$K_c = \bar{K} \pm C_n R$

$K_c = .850 \pm .10$

R = Range = .990 - .747 = .243

C_n for 95% confidence (6 values) = .399

Spectranalized Acetone $CH_3C(O)CH_3$



Solution	C_D°
A	.5045
B	.7696
C	1.0315
D	1.3423

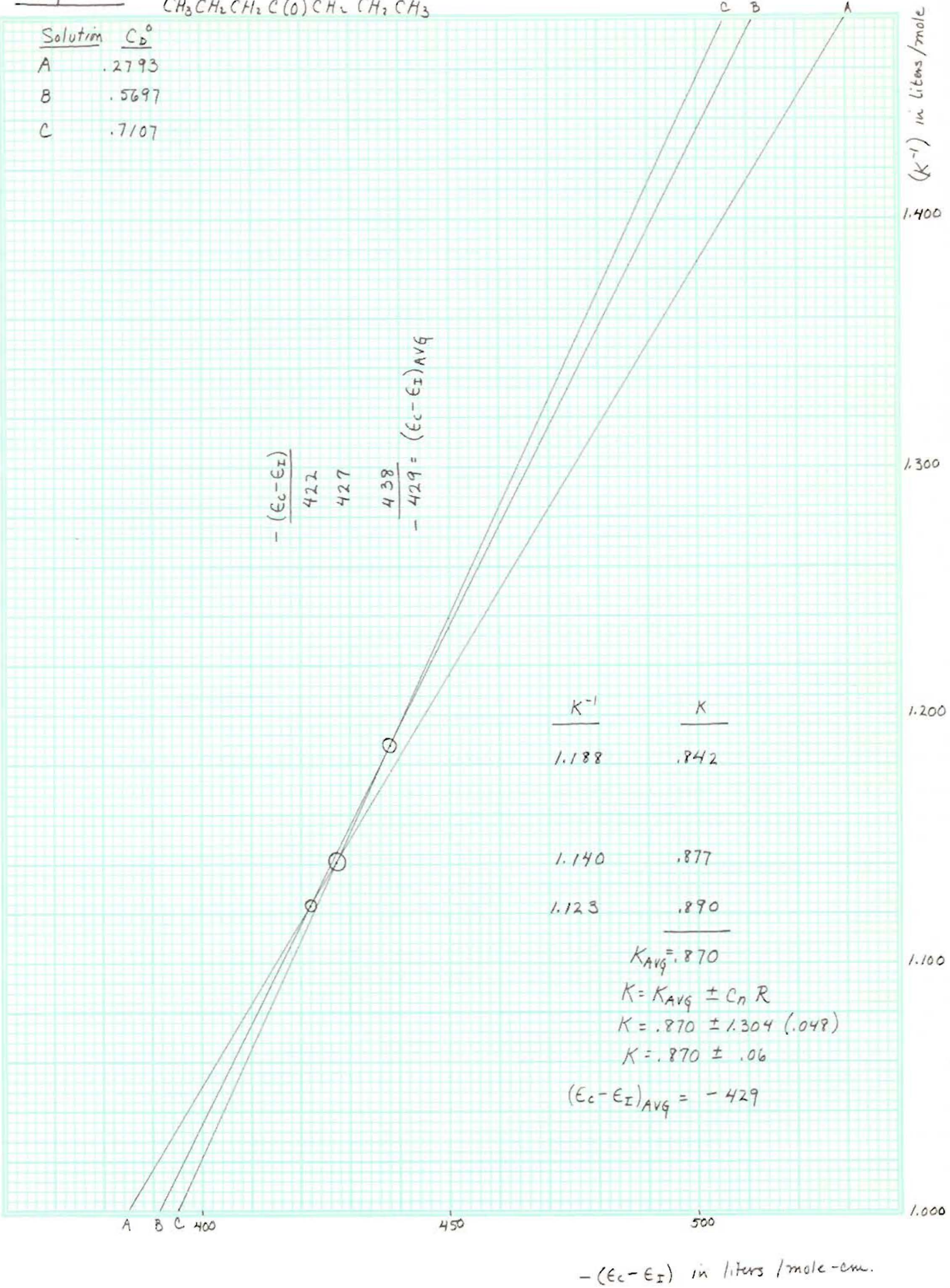
K^{-1}	K
1.338	.747
1.254	.797
1.230	.813
1.154	.867
1.131	.848
1.101	.990

K_{AVG} = .850

$$K = K_{AVG} \pm C_n R$$
$$= .850 \pm .399\,(.243)$$
$$= .850 \pm .10$$

$$(\epsilon_c - \epsilon_I)_{AVG} = {}^{-}510$$

4-Heptanone $CH_3CH_2CH_2C(O)CH_2CH_2CH_3$



Solution	C_D^0
A	.2793
B	.5697
C	.7107

$-(\epsilon_c - \epsilon_I)$
422
427
438
$-429 = (\epsilon_c - \epsilon_I)_{AVG}$

K^{-1}	K
1.188	.842
1.140	.877
1.123	.890

$K_{AVG} = .870$

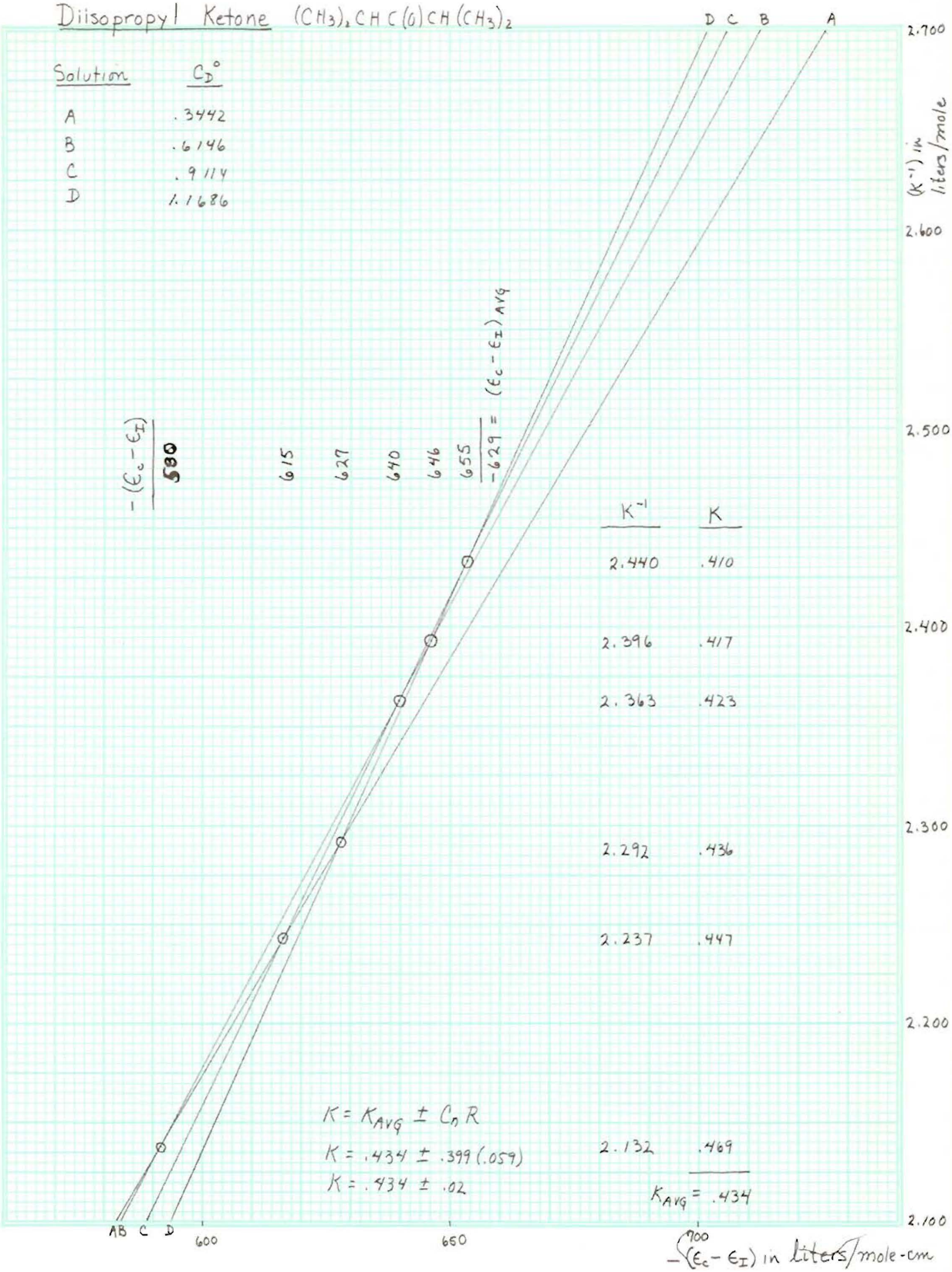
$K = K_{AVG} \pm C_n R$

$K = .870 \pm 1.304\ (.048)$

$K = .870 \pm .06$

$(\epsilon_c - \epsilon_I)_{AVG} = -429$

Diisopropyl Ketone $(CH_3)_2CHC(O)CH(CH_3)_2$



Solution	C_D°
A	.3442
B	.6146
C	.9114
D	1.1686

$-(\epsilon_c - \epsilon_I)$
580
615
627
640
646
655
$-629 = (\epsilon_c - \epsilon_I)_{AVG}$

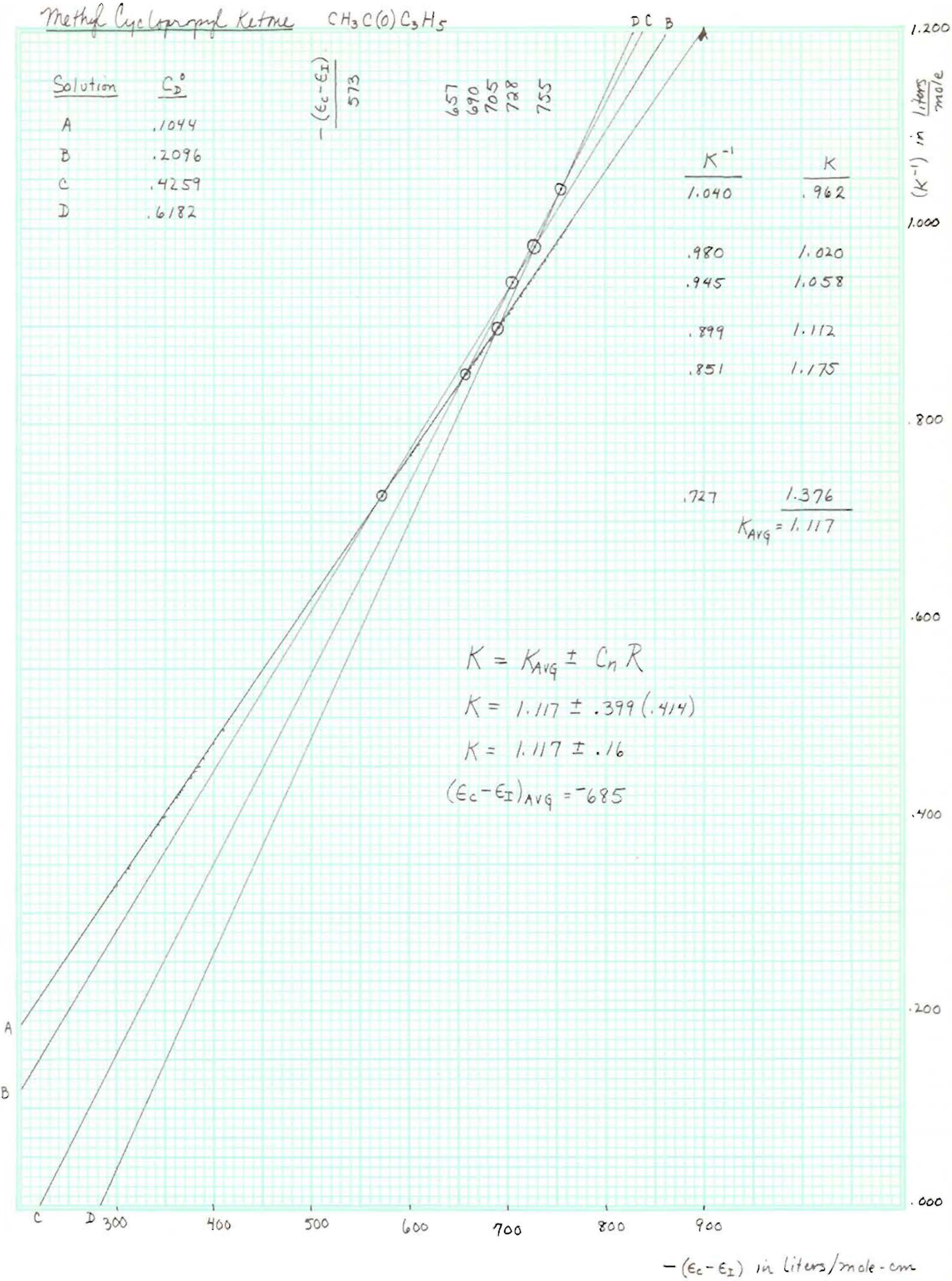
K^{-1}	K
2.440	.410
2.396	.417
2.363	.423
2.292	.436
2.237	.447
2.132	.469
	$K_{AVG} = .434$

$K = K_{AVG} \pm C_n R$

$K = .434 \pm .399(.059)$

$K = .434 \pm .02$

Methyl Cyclopropyl Ketone $CH_3C(O)C_3H_5$



Solution	C_D^0
A	.1044
B	.2096
C	.4259
D	.6182

$-(\epsilon_c - \epsilon_I)$: 573, 657, 690, 705, 728, 755

K^{-1}	K
1.040	.962
.980	1.020
.945	1.058
.899	1.112
.851	1.175
.727	1.376

$K_{AVG} = 1.117$

$K = K_{AVG} \pm C_n R$

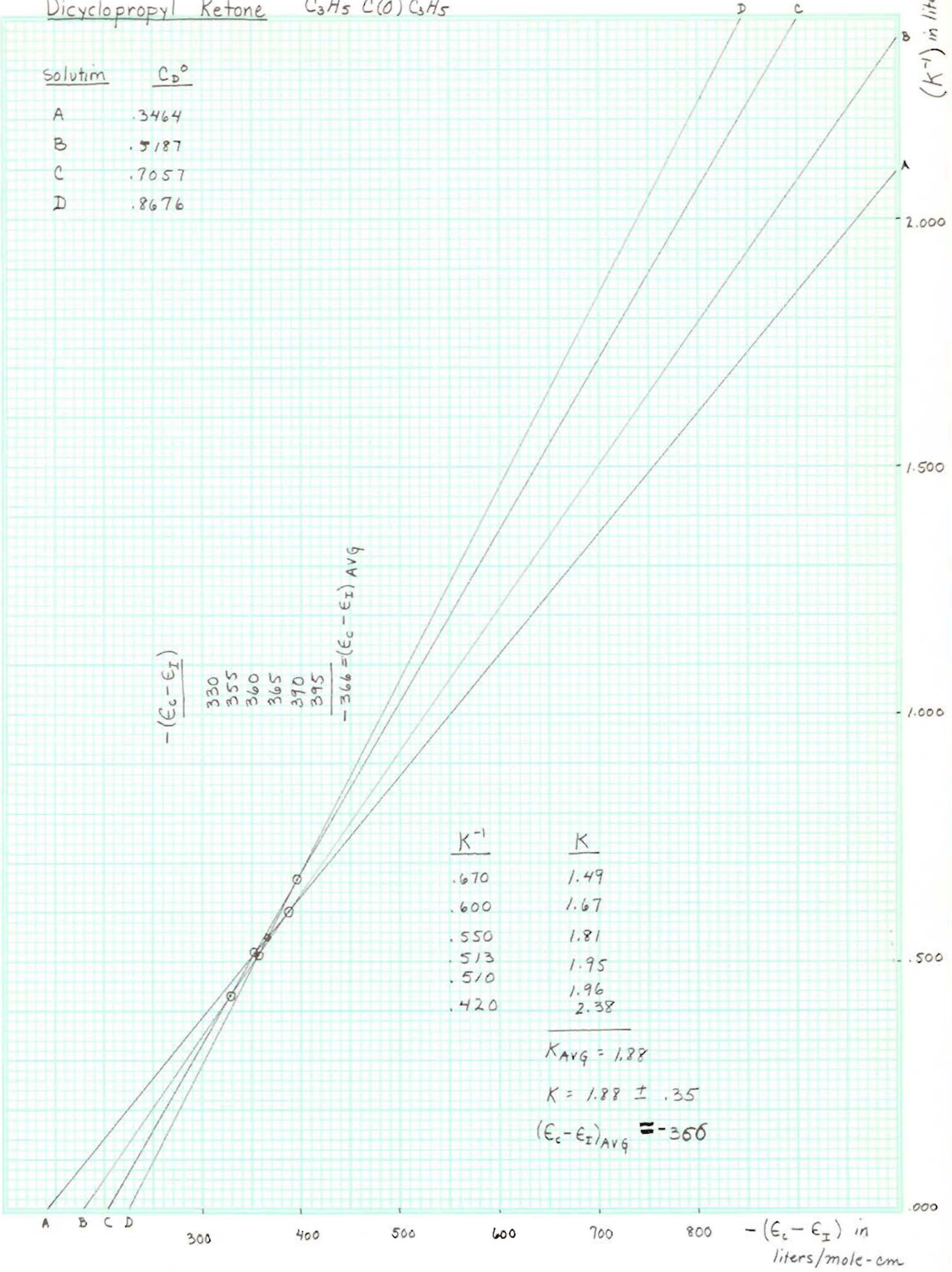
$K = 1.117 \pm .399(.414)$

$K = 1.117 \pm .16$

$(\epsilon_c - \epsilon_I)_{AVG} = {}^-685$

x.

Dicyclopropyl Ketone $C_3H_5C(O)C_3H_5$



Solutim	C_D°
A	.3464
B	.5187
C	.7057
D	.8676

$-(\epsilon_c - \epsilon_I)$
330
355
360
365
390
395

$-366 = (\epsilon_c - \epsilon_I)$ AVG

K^{-1}	K
.670	1.49
.600	1.67
.550	1.81
.513	1.95
.510	1.96
.420	2.38

$K_{AVG} = 1.88$

$K = 1.88 \pm .35$

$(\epsilon_c - \epsilon_I)_{AVG} = -366$