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Relative electronegativities of the propyl groups

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by

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ABSTRACT

Vapor pressure determinations in a vacuum line were made first on varied compositions of acetone and pyridine and second on varied compositions of acetone and trimethylamine. These experiments were conducted in the hope of noting a negative deviation from Raoult's Law, which is indicative of adduct formation between the two substances. No such deviation was found in either case. Vapor pressure determinations were then made on varied compositions of 1) acetone and chloroform, 2) 4-heptanone and chloroform, 3) dicyclopropyl ketone and chloroform, and 4) diisopropyl ketone and chloroform. In each of these systems a negative deviation from Raoult's Law was found, and from these data values for the relative electronegativities of the propyl groups were obtained.

INTRODUCTION

The original title of this paper was intended to be, "Preparation and Characterization of Tricyclopropylaluminum." It was hoped that a preparation of this previously unreported compound, and a measurement of its degree of dimerization, might give evidence as to whether the decrease in dimerization in the homologous trialkylaluminum series is due mainly to steric hindrance[1] or to electronegativity effects of the alkyl group.[2] The tricyclopropylaluminum compound, however, was reported at the fall meeting of the American Chemical Society by Sanders and Oliver of Wayne State University.[3] Their findings show that the tricyclopropylaluminum compound is dimeric, and that, surprisingly, this dimer seems to have the most stable hydrocarbon bridges so far reported in group III derivatives. This report is somewhat contrary to what is expected, and lends added confusion to the problem of steric vs. electronegativity effects.

The present project is still concerned with steric and inductive effects, for it was felt that a study of the relative electronegativities of the propyl groups might reveal some pertinent data in this regard. The experimental work has been carried out in such a manner as to minimize, as much as possible, the steric involvement in the chosen chemical environments. In this way the data obtained are not influenced by steric effects, but represent a true measure of electronegativity effects alone.

In 1957, a study comparing the inductive properties of the cyclopropyl and isopropyl groups (as well as others) was carried out by measuring the intensity of absorption of the O-H group in a series of aliphatic alcohols.[4] This report is based upon the assumption that the intensity of absorption of the O-H group in aliphatic alcohols is determined essentially by the inductive properties of the groups attached to the hydroxyl.[5] The data show that the intensity of absorption for tricyclopropylcarbinol is much greater than that

for triisopropylcarbinol. This observation indicates that the cyclopropyl group is much more electronegative than the isopropyl group, approximately 1.7 times greater,

A more recent article gives a comparison between the relative electronegativities of the cyclopropyl and n-propyl groups.[6] Tricyclopropylphosphine was prepared and its pK_a determined by titration with perchloric acid in nitromethane solution. The pK_a of tricyclopropylphosphine was found to be very nearly the same as that of tri-n-propylphosphine, 7.60 and 7.84 respectively. The smaller the pK_a value, the greater the acid strength, and thus tricyclopropylphosphine is a slightly stronger acid than tri-n-propylphosphine. The conclusion, therefore, is that the cyclopropyl and n-propyl groups have similar electronegativities, the cyclopropyl group being approximately 1.1 times more electronegative than the n-propyl group.

From the above two studies taken together, it can be inferred that the n-propyl group is more electronegative than the isopropyl group. The work by Pitzer and Gutowsky on the trialkylaluminum compounds[1] seems to support this argument. Their findings indicated that tri-n-propylaluminum is partly dimeric in benzene solution, while triisopropylaluminum is completely monomeric. Although these experiments are complicated to a certain extent by steric effects, their results are consistent with the view that the n-propyl group is more electronegative than the isopropyl group.

This project has offered a comparison of the relative electronegativities of the propyl groups by means of vapor pressure determinations in a vacuum line. No similar study of the propyl groups together by a single method has been reported previously. From the above reports it can be presumed that the electronegativities of the propyl groups decrease in the order cyclopropyl> n-propyl>isopropyl. The present work has confirmed this order qualitatively.

It is felt, however, that additional work, particularly gas phase dissociation studies, must be carried out to confirm this order with more certainty and to define quantitatively the relative electronegativities of the propyl groups.

EXPERIMENTAL

1. Purification of Reagents

Acetone - Forty ml of acetone were refluxed over potassium permanganate for thirty minutes and then distilled.[7] Thirty ml were collected over Drierite in a flask which had been previously flushed with nitrogen. The collection temperature was 56.4°C at a pressure of 759.0 mm (lit.[8] : 56.5°C at 760.0 mm). The vapor pressure of the acetone was determined in a vacuum line at six different temperatures between -30°C and 20°C. The values obtained agreed with the literature values.[8] Vapor pressure readings were rechecked at various times during the experimentation to ensure purity.

Pyridine - Thirty ml of pyridine were refluxed over sodium hydroxide pellets for one hour and then distilled.[7] Twenty ml were collected over Drierite in a flask which had been previously flushed with nitrogen. The collection temperature was 115.8°C at a pressure of 762.5 mm (lit.[8] : 115.3°C at 760.0 mm). The vapor pressure of pyridine was determined at 0°, 10°, and 20°C, and these values agreed with the literature values.[8] These readings were also rechecked at various times.

4-Heptanone - Twenty ml of 4-heptanone were refluxed over Drierite for thirty minutes and then distilled. A middle fraction of 10 ml was collected over Drierite in a flask which had been previously heated and allowed to cool with a drying tube inserted. The collection temperature was 143-144°C at a pressure of 764.2 mm (lit.[8] : 144°C at 760.0 mm).

Dicyclopropyl ketone - Thirty ml of dicyclopropyl ketone were refluxed over Drierite for one hour and then distilled. A middle fraction of 20 ml was collected over Drierite in a flask which had been previously flushed with nitrogen. The collection temperature was 163-164°C at a pressure of 756.2 mm (lit.[9] : 162.5-163.0°C at 760.0 mm).

Diisopropyl ketone - Thirty ml of diisopropyl ketone were refluxed over Drierite for one hour and then distilled. A middle fraction of 20 ml was collected over Drierite in a flask which had been previously flushed with nitrogen. The collection temperature was 122-123°C at a pressure of 760.5 mm (lit.[8] : 123.7°C at 760.0 mm).

Chloroform - Fifty ml of chloroform were shaken three times with a small volume (about 5%) of concentrated sulfuric acid, and then thoroughly washed with water.[7] Thirty ml were refluxed for one hour over Drierite and then distilled. Twenty ml were collected over Drierite in a flask which had been previously flushed with nitrogen. The collection temperature was 59.0-59.7°C at a pressure of 750.0 mm (lit.[8] : 61.26°C at 760.0 mm).

2. Calibration of Traps on the Vacuum Line

The three traps on the vacuum line were calibrated by introducing a known amount of carbon dioxide into the first trap, reading the pressure and computing the volume by means of the ideal gas law. The gas was then allowed to expand into the other two traps, one at a time, and similar calculations were made. This procedure was repeated six times, and a plot of the values, pressure vs. volume, gave straight lines for each of the three calibrations.

3. Vapor Pressure Determinations of Mixtures of Acetone and Pyridine

Vapor pressure determinations in a vacuum line were carried out at 0°C while varying the composition of acetone and pyridine. By using two different samples, vapor pressure readings were taken as the mole fraction of acetone was decreased from 0.90 to 0.20. Acetone was removed by putting a chloroform slush bath (-63°C) around the trap containing the mixture of acetone and pyridine, and liquid nitrogen (-196°C) around a second trap. The vapor pressure vs. composition data are recorded in Table 1 and are plotted on Graph 1.

Table 1

Pressure above Acetone - Pyridine Solution at 0°C.

Mole Fraction of Acetone	P, mm, Exptl.	P, mm, Theor.
1.000	71.7	69.2
.898	63.0	62.2
.893	62.7	62.0
.840	59.0	58.2
.801	57.2	55.9
.768	57.1	53.8
.761	56.0	53.2
.747	56.0	52.2
.712	52.8	50.1
.682	50.9	48.2
.633	48.4	45.0
.564	44.3	40.5
.493	40.0	35.8
.464	38.0	34.0
.415	35.0	30.7
.360	31.6	27.2
.290	28.1	22.7
.229	24.3	18.7
.191	21.1	16.1
.000	4.0	4.1

4. Vapor Pressure Determinations of Mixtures of Acetone and Trimethylamine

Vapor pressure determinations in a vacuum line were carried out at 0°C while varying the composition of acetone and trimethylamine. After preliminary data were gathered it was found that the results were not useful for the present study, and no further determinations were made.

5. Vapor Pressure Determinations of Mixtures of Acetone and Chloroform

Vapor pressure determinations in a vacuum line were carried out at 0°C while varying the composition of acetone and chloroform. Two runs were made, and a cathetometer was used in this experiment as well as in experiments 6, 7, and 8. In the first run the mole fraction of acetone was increased from 0.00 to 0.74 by adding acetone, and in the second the mole fraction of

acetone was decreased from 1.00 to 0.23 by adding chloroform. The vapor pressure vs. composition data are recorded in Table 2. and are also plotted on Graph 2.

Table 2.

Pressure above Acetone - Chloroform Solution at 0°C.

Mole Fraction of Acetone	P, mm, Exptl.	P, mm, Theor.
1.000	70.3	69.2
.827	63.2	67.8
.737	58.9	67.0
.712	58.7	66.9
.645	54.2	66.2
.624	54.0	66.1
.594	53.0	65.9
.556	51.0	65.5
.527	50.2	65.2
.502	49.0	65.1
.434	47.7	64.6
.421	47.8	64.5
.365	46.4	64.0
.316	47.9	63.5
.277	47.8	63.2
.231	48.4	62.9
.160	52.2	62.2
.000	61.4	61.0

6. Vapor Pressure Determinations of Mixtures of 4-Heptanone and Chloroform

Vapor pressure determinations in a vacuum line were carried out at 0°C while varying the composition of 4-heptanone and chloroform. Three runs were made and the mole fraction of 4-heptanone was decreased from 1.00 to 0.10. The vapor pressure vs. composition data are recorded in Table 3. and are also plotted on Graph 3.

Table 3

Pressure above 4-Heptanone - Chloroform Solutions at 0°C.

Mole Fraction of 4-Heptanone	P, mm, Exptl.	P, mm, Theor.
1.000	0.1	0.1
1.000	0.1	0.1
.812	5.7	11.9
.683	10.9	19.8
.593	14.7	25.2
.592	14.8	25.2
.518	19.4	30.0
.463	23.3	33.3
.419	26.8	36.0
.381	28.0	38.3
.325	32.8	41.9
.301	37.3	43.2
.266	37.6	45.4
.225	43.1	48.0
.207	39.7	49.1
.195	45.3	49.8
.179	48.2	50.8
.172	49.1	51.1
.158	49.9	52.1
.141	49.8	53.1
.104	54.1	55.3

7. Vapor Pressure Determinations of Mixtures of Dicyclopropyl Ketone and Chloroform

Vapor pressure determinations in a vacuum line were carried out at 0°C while varying the composition of dicyclopropyl ketone and chloroform. Four runs were made and the mole fraction of dicyclopropyl ketone was decreased from 1.00 to 0.08. The vapor pressure vs. composition data are recorded in Table 4 and are also plotted on Graph 4.

Table 4.

Pressure above Dicyclopropyl Ketone - Chloroform Solutions at 0°C.

Mole Fraction of Dicyclopropyl Ketone	P, mm, Exptl.	P, mm, Theor.
1.000	1.3	---
1.000	0.2	---
.781	5.5	14.4
.642	15.2	22.7
.588	20.6	25.8
.544	15.3	28.4
.483	21.7	32.0
.472	20.0	32.5
.373	27.6	38.7
.319	33.0	41.8
.284	37.0	43.9
.251	38.5	45.9
.238	44.2	46.8
.183	47.5	49.8
.159	48.0	51.3
.158	52.4	51.3
.132	55.3	52.7
.127	54.7	53.2
.084	56.7	55.6

8. Vapor Pressure Determinations of Mixtures of Diisopropyl Ketone and Chloroform

Vapor pressure determinations in a vacuum line were carried out at 0°C while varying the composition of diisopropyl ketone and chloroform. Six runs were made and the mole fraction of diisopropyl ketone was decreased from 1.00 to 0.06. The vapor pressure vs. composition data are recorded in Table 5 and are plotted on Graph 5.

Table 5.

Pressure above Diisopropyl Ketone - Chloroform Solutions at 0°C.

Mole Fraction of Diisopropyl Ketone	P, mm, Exptl.	P, mm, Theor.
1.000	2.8	0.7
1.000	6.7	0.7
1.000	4.6	0.7
1.000	2.9	0.7
1.000	2.6	0.7
.873	3.9	8.9
.801	9.3	13.1
.775	6.0	14.8
.696	9.1	19.5
.687	8.4	20.0
.668	12.1	21.0
.579	15.6	26.5
.572	17.4	26.5
.544	16.8	28.3
.523	15.1	29.7
.518	16.5	30.0
.501	21.2	30.8
.495	21.5	31.3
.439	23.1	34.8
.401	25.8	36.9
.385	28.3	37.9
.373	29.1	38.4
.348	30.4	40.1
.284	37.2	43.9
.229	41.2	47.1
.166	48.6	51.0
.127	51.5	53.2
.062	56.1	56.9

9. Calculation of Relative Electronegativities of Methyl and Propyl Groups

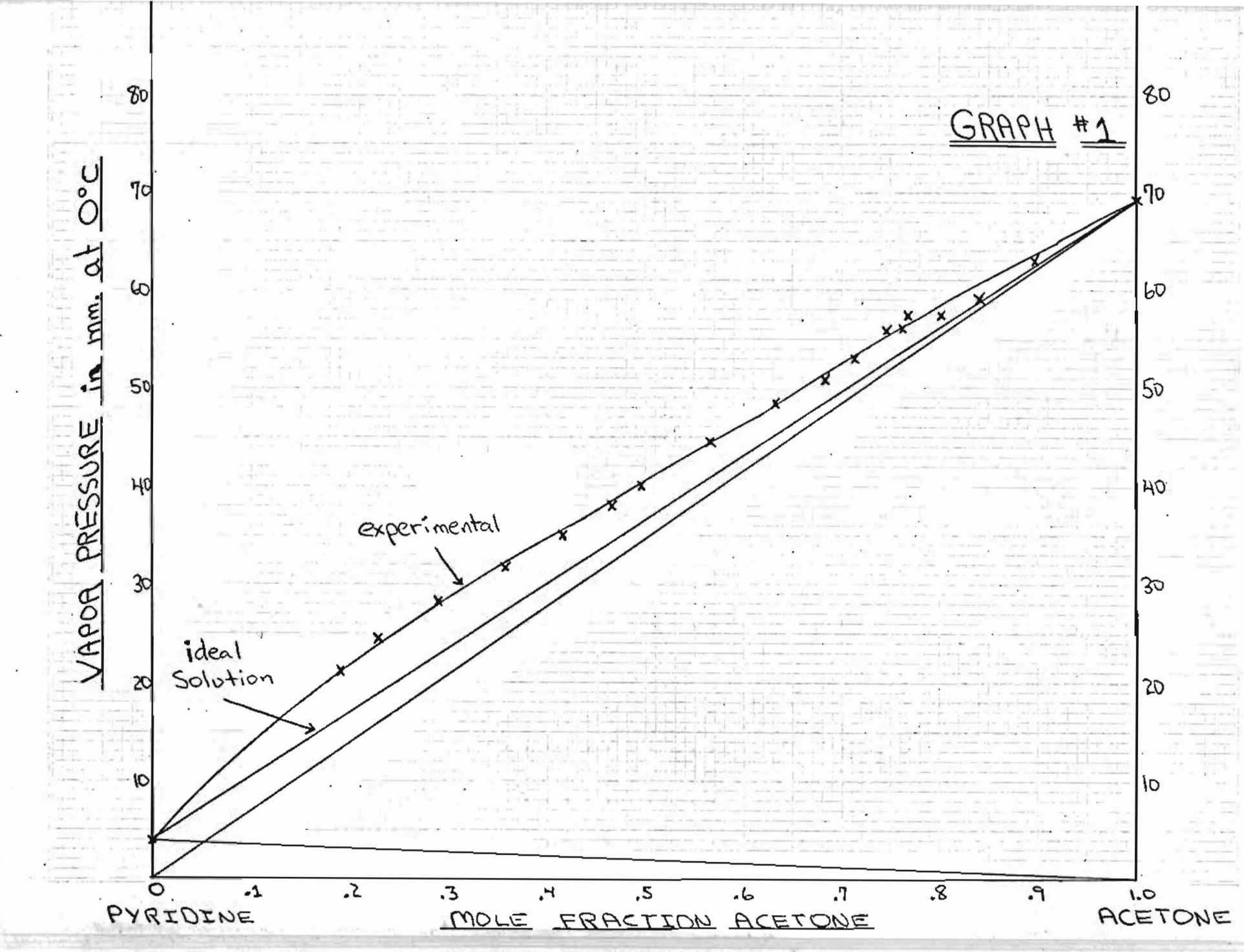
The relative electronegativities of the methyl and propyl groups were calculated by first taking eleven points along the abscissa on graphs 2, 3, 4, and 5. At each mole fraction value the deviation from the ideal curve was measured and its fraction of the total distance found. For each graph these eleven values were then added together and the reciprocal taken, since the

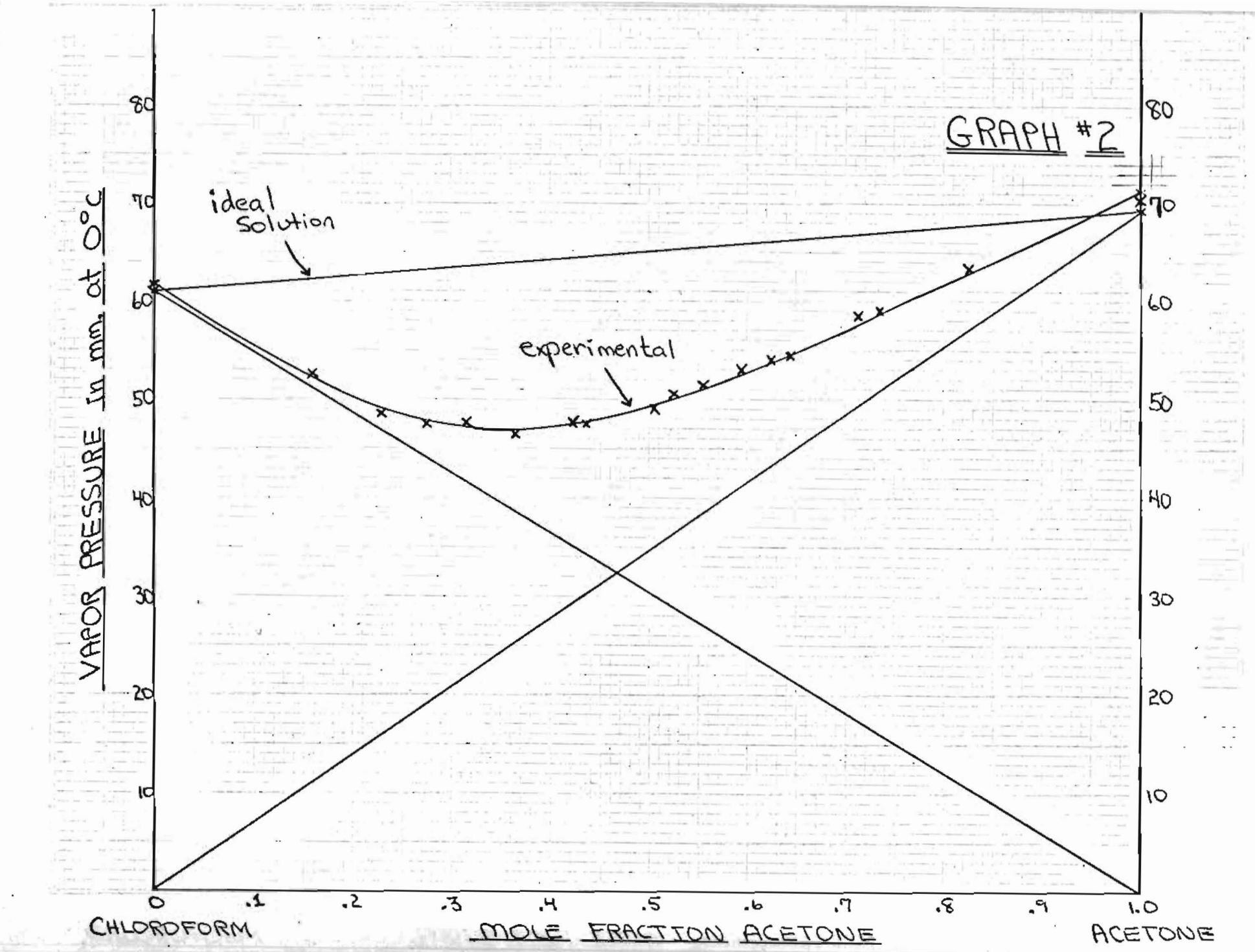
deviation, a measure of the amount of adduct formation, is inversely proportional to the relative electronegativity. The electronegativity of the isopropyl group was assigned a value of 1.00, and the relative electronegativities of the other groups were calculated from this assigned value. The data are recorded in Table 6.

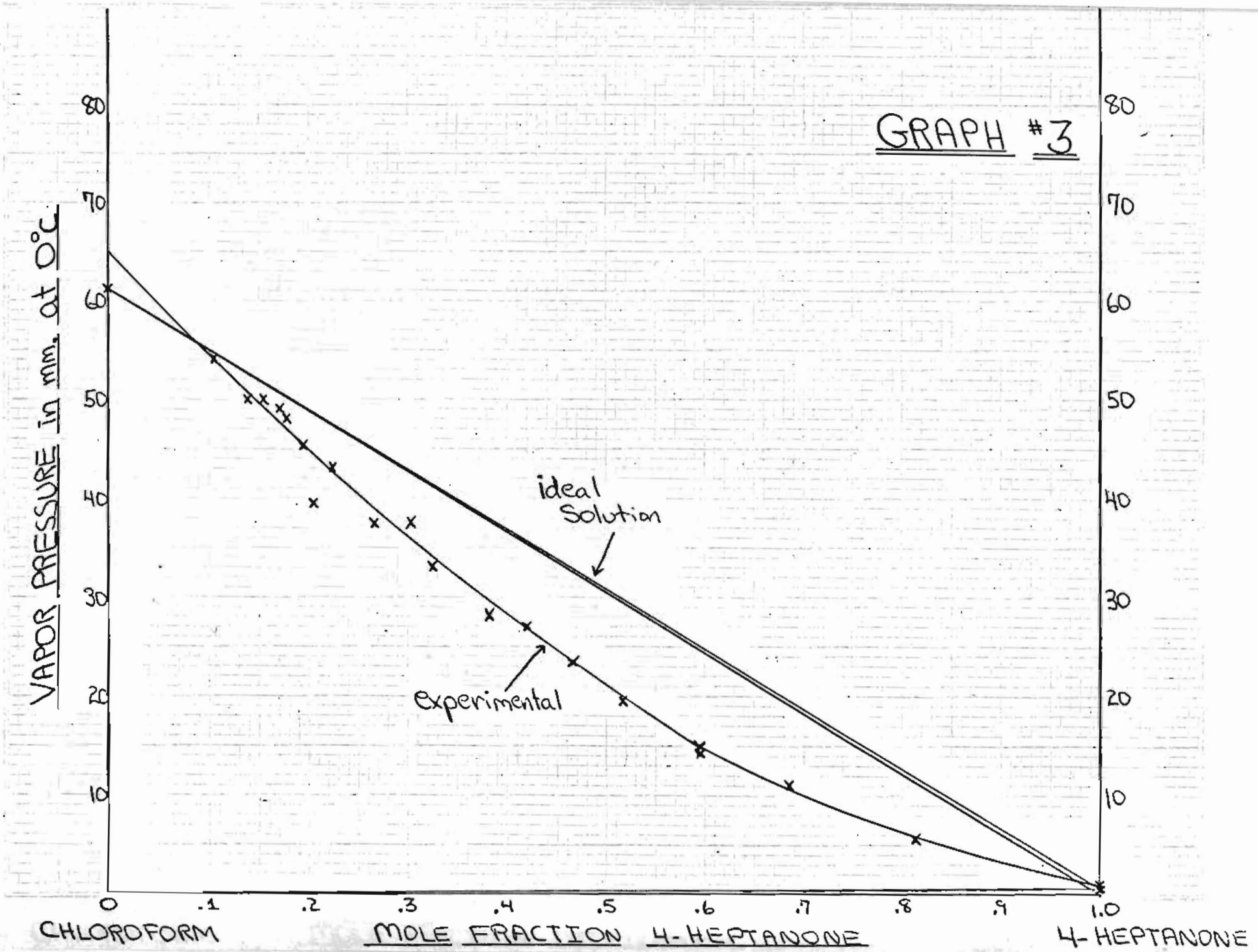
Table 6

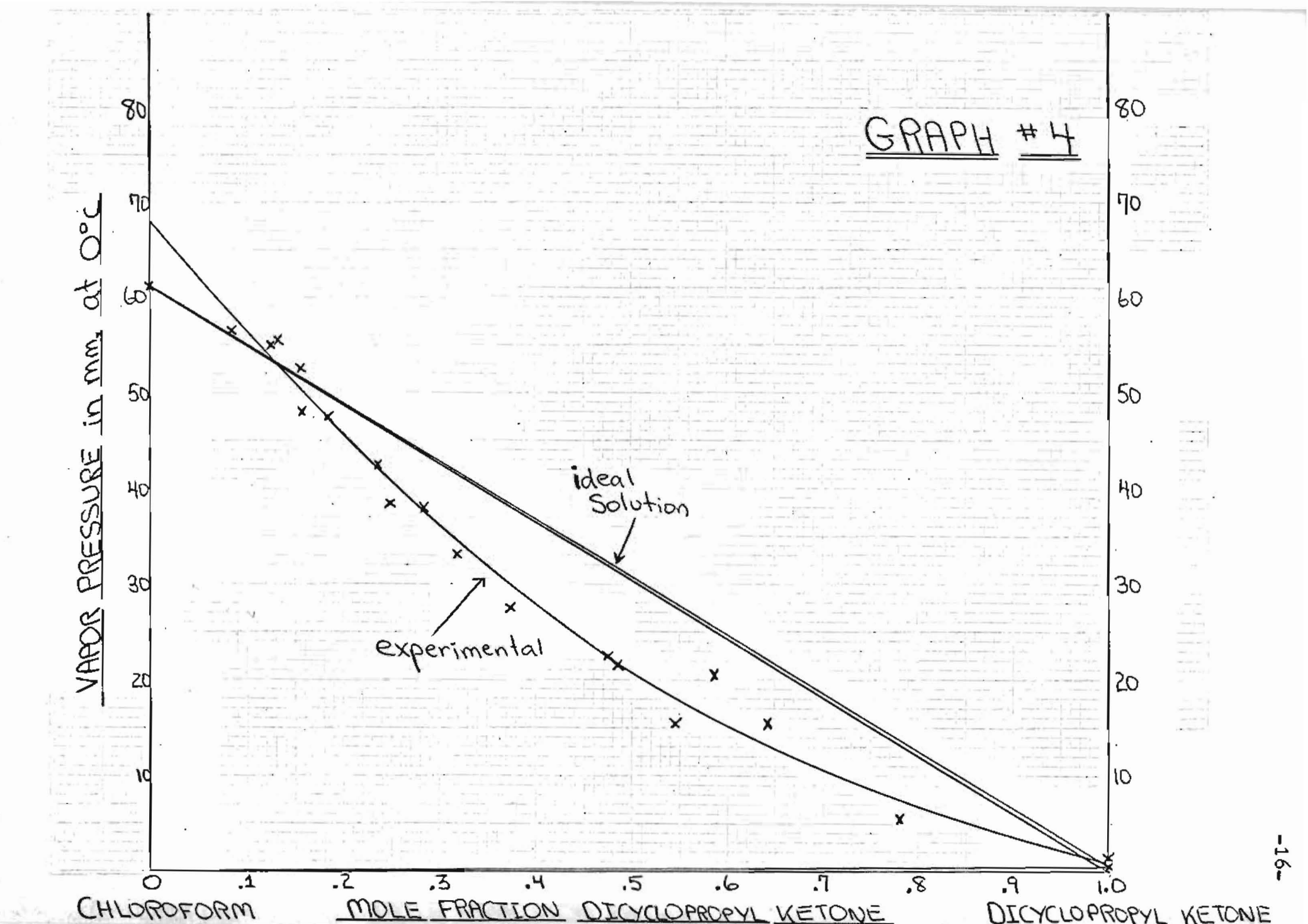
Relative Electronegativities of Methyl and Propyl Groups

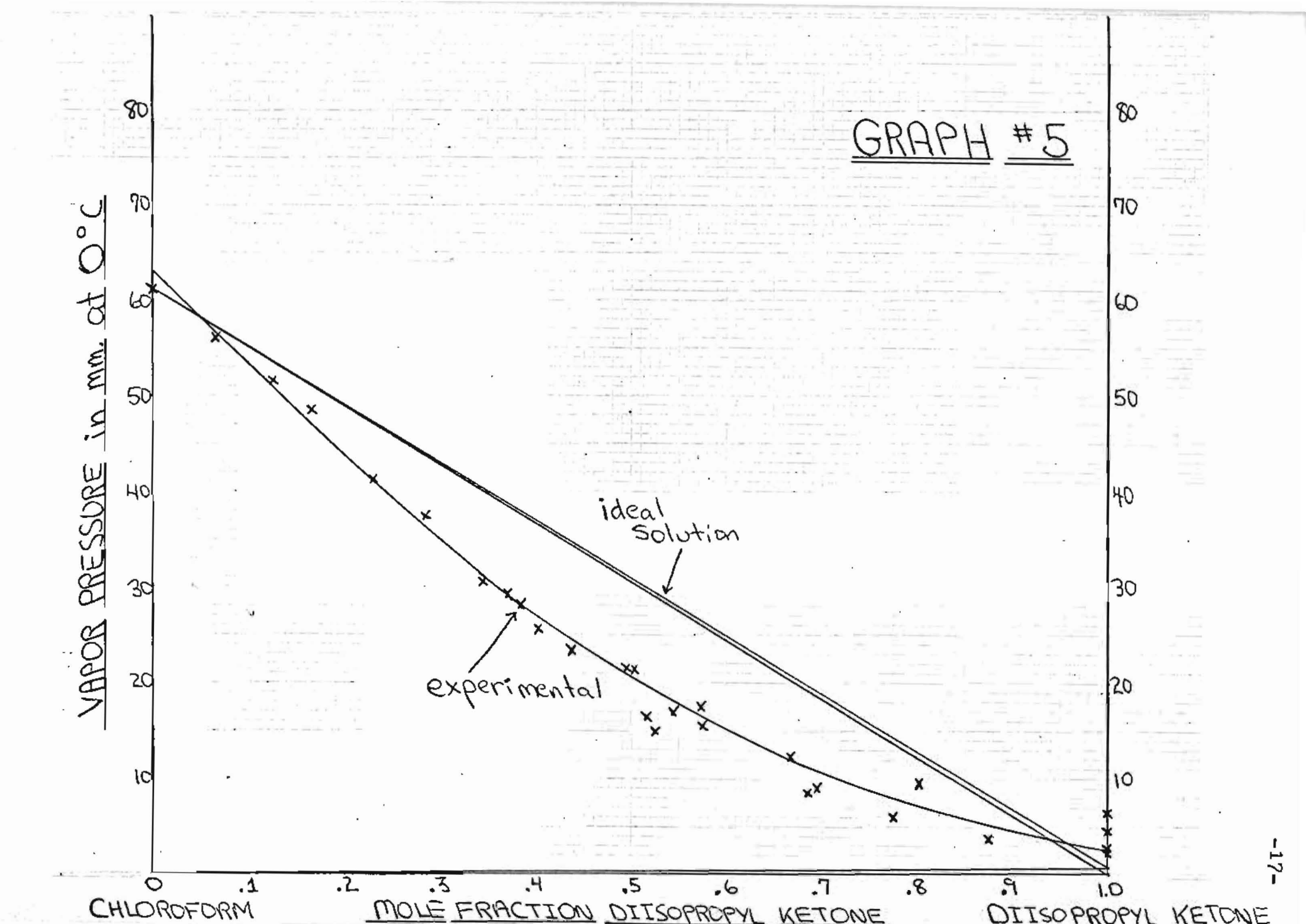
Mole Fraction of Ketone	Deviation from Ideal Pressure over Ideal Pressure (x10)			
	Acetone	4-Heptanone	Diisopropyl Ketone	Dicyclopropyl Ketone
0.90	5.0/136=0.37	9.0/13.5=6.67	6.0/14.5=4.14	6.5/15.0=4.33
0.80	11.5/134=0.86	12.0/25.5=4.71	14.5/26.5=5.47	11.5/27.0=4.26
0.70	20.0/132=1.51	17.0/38.0=4.47	20.0/38.0=5.26	15.5/38.5=4.03
0.60	26.0/131=1.98	19.0/50.0=3.80	22.0/50.0=4.40	18.5/50.5=3.66
0.55	28.5/130=2.18	19.5/56.0=3.48	23.0/55.5=4.14	19.5/56.5=3.45
0.50	31.5/130=2.43	19.0/62.0=3.06	23.0/62.0=3.71	19.5/62.0=3.14
0.45	33.0/129=2.56	18.0/68.5=2.63	22.5/67.5=3.33	19.5/68.0=2.87
0.40	34.5/128=2.71	18.0/74.5=2.42	21.0/73.5=2.86	18.5/74.0=2.50
0.30	32.5/126=2.58	14.5/87.0=1.67	16.0/85.0=1.88	15.0/86.0=1.74
0.20	25.0/124=2.01	9.0/98.5=0.91	9.0/97.0=0.93	7.0/97.5=0.72
0.10	12.0/123=0.98	1.5/111 =0.14	2.5/109 =0.23	-3.5/110=-0.32
TOTAL	20.17	33.96	36.35	30.38
100/T	4.96	2.94	2.75	3.29
Relative Electronegativities	1.80 (methyl)	1.07 (n-propyl)	1.00 (isopropyl)	1.20 (cyclopropyl)


GRAPH #1
VAPOR PRESSURE in mm. at 0°C
80
70
60
50
40
30
20
10
experimental
ideal
Solution
0
.1
.2
.3
.4
.5
.6
.7
.8
.9
1.0
PYRIDINE
MOLE FRACTION ACETONE
ACETONE


GRAPH #2
VAPOR PRESSURE in mm. at 0°C
80
70
60
50
40
30
20
10
ideal solution
experimental
0
.1
.2
.3
.4
.5
.6
.7
.8
.9
1.0
CHLOROFORM
MOLE FRACTION ACETONE
ACETONE


GRAPH #3
VAPOR PRESSURE in mm. at 0°C.
80
70
60
50
40
30
20
10
ideal Solution
experimental
0
.1
.2
.3
.4
.5
.6
.7
.8
.9
1.0
CHLOROFORM
MOLE FRACTION 4-HEPTANONE
4-HEPTANONE


GRAPH #4
VAPOR PRESSURE in mm. at 0°C
80
70
60
50
40
30
20
10
ideal Solution
experimental
0
.1
.2
.3
.4
.5
.6
.7
.8
.9
1.0
CHLOROFORM
MOLE FRACTION DICYCLOPROPYL KETONE
DICYCLOPROPYL KETONE


GRAPH #5
VAPOR PRESSURE in mm. at 0°C
80
70
60
50
40
30
20
10
ideal
Solution
experimental
0
.1
.2
.3
.4
.5
.6
.7
.8
.9
1.0
CHLOROFORM
MOLE FRACTION DIISOPROPYL KETONE
DIISOPROPYL KETONE

CONCLUSIONS and SUGGESTIONS

From the vapor pressure vs. composition experiments between acetone and pyridine and between acetone and trimethylamine, it can be concluded that there is no adduct formation in either system. In the acetone-pyridine system the positive deviation from the Raoult's Law curve, the ideal solution curve, indicates that there may, in fact, be some repulsion. Since the dipropyl ketones should all be weaker Lewis acids than acetone, it was assumed that they too would not form adducts with either pyridine or trimethylamine. The degree of adduct formation is a measure of the acid strength, which, assuming other effects are negligible, is a means of indicating the relative electronegativities of the various propyl groups.

Since the dipropyl ketones were too weak Lewis acids to form adducts, another attempt to measure relative electronegativities of the propyl groups was made by using the dipropyl ketones as Lewis bases. The electrons on the oxygen are available for bonding, and thus the ketones can act as electron donors. The Lewis acid which was used was chloroform, which is known to form adducts with acetone,[10] with di-n-propyl ketone (4-heptanone),[11] and with diisopropyl ketone (2,4-dimethyl-3-pentanone).[10] The existence of an adduct between chloroform and dicyclopropyl ketone has not been reported in the literature. The formation of hydrogen bonds in the adduct is apparently hindered in no way by steric effects, as is evident from models, and therefore this adduct with chloroform has been an ideal one in which to study electronegativity effects alone.

The vapor pressure vs. composition experiments between 1) acetone and chloroform, 2) 4-heptanone and chloroform, 3) dicyclopropyl ketone and chloroform, and 4) diisopropyl ketone and chloroform have shown in each case that there is a negative deviation from the Raoult's Law curve. It has thus been con-

cluded that in each of these four systems there is adduct formation between chloroform and the various ketones. The greater the extent of adduct formation, the greater is the resulting deviation from the ideal solution curve. The greater the extent of adduct formation, the smaller is the electronegativity of the group, i.e. the greater is the feed of electrons toward the site of hydrogen bonding. Thus the amount of deviation is inversely proportional to the relative electronegativity. It is on this basis that the relative electronegativities of the propyl groups have been calculated. In order of decreasing electronegativity the following series has been found: cyclopropyl>n-propyl> isopropyl, with the ratio being 1.20 : 1.07 : 1.00. This ratio for the relative electronegativities must be considered, however, only a qualitative estimate, and more work is needed to establish the precise values.

This order agrees nicely with Gillespie's explanation of dimerization in the trialkylaluminum compounds.[12] His argument rests on the assumption that the more electronegative group will bring out the highest coordination number of aluminum. Thus the greater the electronegativity, the greater the extent of association in the organoaluminum compounds. The extent of dimerization decreases in the order tricyclopropylaluminum>tri-n-propylaluminum>triisopropylaluminum. This order agrees with the order of electronegativities stated above. The extent of association in tricyclopropylaluminum is also greater than that in trimethylaluminum. This implies that the cyclopropyl group is more electronegative than the methyl group. According to the vapor pressure vs. composition experiments conducted in this project, the opposite was found to be the case, i.e. the methyl group is more electronegative than the cyclopropyl group (1.80 : 1.20). It must be stated again, however, that this work can be considered only qualitative, and that further study is needed to obtain truly quantitative values.

It is felt that gas phase dissociation studies between chloroform and the various ketones will prove fruitful in obtaining more accurate values for the relative electronegativities. Through the ~~obtainment~~ obtaining of equilibrium constants, one should have the quantitative tools to prove whether the methyl or cyclopropyl group is more electronegative and also to establish precise values for the relative electronegativities of the propyl groups.

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