THE SURFACE TENSION AND VAPOR PRESSURE OF LIQUID MIXTURES OF THE COTTONSEED OIL - ETHYL ACETATE SYSTEM AND THE MOLECULAR WEIGHT OF COTTONSEED OIL

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CONTENTS

	Page
Summary	1
Introduction	3
Materials and Equipment	8
Figures 1 and 2	12-13
Procedure	14
Discussion of Results	19
Tables I and II	24-26
Figures 3, 4, 5, 6, 7, 8	27-32
Conclusions and Recommendations	33
Bibliography	35
Appendix A	36
Appendix B	47
Acknowledgment	52
Approval	53

THE SURFACE TENSION AND VAPOR PRESSURE OF LIQUID MIXTURES OF THE COTTONSEED OIL - ETHYL ACETATE SYSTEM AND THE MOLECULAR WEIGHT OF COTTONSEED OIL

SUMMARY

Studies were to be made in the University of Tennessee's Department of Chemical Engineering concerning the mechanism of stripping ethyl acetate, a volatile substance from non-volatile cottonseed oil. Variables to be evaluated in these studies were the surface tension and vapor pressure of liquid mixtures of the system and the molecular weight of cottonseed oil. This investigation involved the determination of the absolute surface tension in dynes per centimeter and the vapor pressure in millimeters of mercury of the cottonseed oil - ethyl acetate system as a function of temperature and composition. The absolute surface tension, the vapor pressure and the molecular weight were determined by a model No. 70540 Cenco-du Nouy Interfacial Tensiometer, the static-head method, and the lowering-of-the-freezing-point method, respectively.

The surface tension was obtained for eleven compositions over the temperature range 20° to 60° C. The temperatures were plotted against the surface tensions, and lines

connecting points of approximately equal compositions were drawn. Compositions were plotted against surface tensions, and curves connecting the points of equal temperatures were drawn. It was found that a maximum surface tension occurred at a composition of about 20 mole percent ethyl acetate. The equation of line relating refractive index to composition was found by the method of "least squares" to be:

$$Y = -9.755 \times 10^{-4} + 1.4705$$

Y = refractive index, units based on air.

X = concentration ethyl acetate in weight percent.

The vapor pressure was obtained for seven compositions over the temperature range 20 to 60° C. The logarithm of the vapor pressures was plotted against the reciprocal of the absolute temperature, and the slope and intercept were obtained for each composition. The molecular weight of the cottonseed oil was found to be 828 by plotting the determined molecular weights against the weights of solute added to the solvent and extrapolating to infinite dilution.

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INTRODUCTION

The surface tension and vapor pressure of a solution of cottonseed oil and ethyl acetate were variables and the molecular weight of cottonseed oil was an unknown necessary in the study of stripping ethyl acetate, a volatile substance, from non-volatile cottonseed oil. The purpose of this investigation was to determine the surface tension and the vapor pressure of liquid mixtures of this system as a function of temperature and composition and to determine the molecular weight of cottonseed oil.

Surface Tension

The attraction between the molecules of a liquid manifests itself near the surface where the molecules are subject to an unbalanced force. The molecules of the surface are pulled inward by the other molecules of the liquid, and the liquid tends to adjust itself to give a minimum surface area. The surface tension of a liquid is a force per unit area on the surface of a liquid which opposes the expansion of that area.

The surface tension of a liquid decreases as the temperature rises and the molecular agitation increases. At the critical temperature, where the liquid becomes indistinguishable from a gas, the surface tension should become negligible. The following relation was developed by Eotvos, Ramsey, and Shields. (5)

$$\gamma(Mv)^{2/3} = k(t_c - t - 6)$$

Mv = volume of a gram mole of the liquid

t = temperature of the experiment, °C.

t_c = critical temperature, °C.

k = constant

M = molecular weight of the liquid

v = volume of one gram of liquid

γ = surface tension in dynes per centimeter

This is an empirical equation for pure liquids only.

The constant, k, can be calculated as follows: (7)

$$k = \frac{\left(\frac{M}{d_1}\right)^{2/3} - \left(\frac{M}{d_2}\right)^{2/3}}{t_2 - t_1}$$

γ_1 and γ_2, d_1 and d_2, are respectively the surface tensions and densities of the pure liquid at the temperatures t_1 and t_2, respectively.

There has been little or no advancements pretaining to the theoretical relationship of solution mixtures with

surface tension and the temperature of the solution.

Vapor Pressure

"According to the kinetic theory there is a continuous flight of molecules from the surface of a liquid into the free space above it. At the same time molecules of vapor return to the surface of the liquid at a rate depending on the concentration of the vapor. Eventually a condition of equilibrium is established between the liquid and its vapor, when the rate of escape is exactly equal to the rate of condensation of vapor. The pressure exerted by vapor which is in equilibrium with the liquid is known as the vapor pressure. The equilibrium between a liquid and its vapor is dependent upon the temperature. For every temperature below the critical temperature, there is a certain pressure at which vapor and liquid may exist in equilibrium in all proportions; and, conversely, for every pressure below the critical pressure, there is a certain temperature at which vapor and liquid may exist in equilibrium in all proportions. The vapor pressure of a liquid is a constant quantity at any temperature and is independent of the amounts of liquid and vapor present but it increases as the temperature is raised." (3)

If a liquid is placed in a container and the container is connected to a vacuum pump and a manometer, the vapor pressure of the liquid may be determined by evacuating the system.

After disconnecting the pump, thus isolating the system, the liquid will vaporize until the vapor is in equilibrium with it. This is the vapor pressure at that temperature. The temperature of the liquid may be changed and its vapor pressure obtained after enough time has been allowed for equilibrium to be reached.

When the vapor pressures of one concentration of original liquid are plotted against the reciprocal of the corresponding absolute temperatures a relation may be obtained which will allow the vapor pressure at any temperature to be calculated, or vice versa, for that concentration. If the vapor pressure is plotted as the ordinate and the reciprocal of the absolute temperature is plotted as the abscissa or semi-logarithmic paper and if a straight line results, the equation is of the form:

$$\log P = \frac{A}{T} + B$$

where

P = vapor pressure

T = absolute temperature

A = the slope of the line, a constant

B = the intercept of the line, a constant.

Molecular Weight

It has long been known that the freezing point of water, or other liquids, is lowered by the addition of a solute,

and it was pointed out by Blagden more than a century ago that the depression of the freezing point is directly proportional to the concentration of the solution. It has been shown (4) that this relation for dilute solutions is:

$$\Delta T_f = K_f \frac{W_2}{M_2} \times \frac{1000}{W_1}$$

where

ΔT_f = the change between the freezing point of the original solvent and the freezing point of the solution.

K_f = an experimentally determined constant, dependent solely on the solvent; the molal depression constant.

W_2 = the weight of solute added to lower the freezing point by ΔT_f.

W_1 = the original weight of solvent.

M_2 = the molecular weight of the solute.

Hence, the molecular weight of the solute may be determined if the freezing point lowering, the weight of solute added, the original weight of solvent and the molal depression constant are known. The molal depression constant of most ordinary solvents may be found in the handbooks. (6) Those for benzene and water are 5.12 and 1.86, respectively.

MATERIALS AND EQUIPMENT

Surface Tension

The purified cottonseed oil was manufactured by the Lookout Oil Co., Chattanooga, Tennessee. The ethyl acetate contained 0.005 percent non-volatile impurities and was manufactured by the General Chemical Co., New York, N. Y. A mercury thermometer was used for temperature measurements. Its range was from minus 20° C. to plus 110° C., plus or minus one degree. A small electrical stove was used to heat the cottonseed oil - ethyl acetate solution above 30° C., and a Petri cup was used to hold the sample during surface tension measurements.

The Cenco-du Nouy Tensiometer, model number 70540, was manufactured by the Central Scientific Co., Chicago, Illinois. It was accurate to ± 0.1 dyne per centimeter over a range of ± 100 dynes per centimeter. Reference is made to the literature (2) for further information regarding this instrument. A six centimeter platinum ring, model number 70542, was used in conjunction with the tensiometer.

The Abbe Refractometer was used to obtain the refractive index of the solutions. It was manufactured by Bausch and Lomb Optical Company, Rochester, N. Y. It was accurate to ± 0.0001 units based on air. Two lengths of five feet hose, and one length of one half foot soft rubber hose were used to

maintain a constant water bath temperature with the connections on the refractometer and a hot and cold dual water connection. Further reference is made to the literature for details of the refractometer. (1)

Vapor Pressure (Refer to Figure 1)

The purified cottonseed oil was manufactured by the Lookout Oil Company, Chattanooga, Tennessee. The ethyl acetate containing 0.005 percent non-volatile impurities was manufactured by the General Chemical Company, New York, N. Y. Undistilled water was used for the water bath.

The equipment consisted of a vacuum pump, a bomb, a manometer and accessories. The pump was manufactured by the G. F. Nelson Vacuum Pump Company, Berkeley, California and was driven by a 1/4 hp., 110 volt A. C., single phase motor. The bomb was made from a $1\frac{1}{2}$ inch brass pipe six inches in length sealed at one end with a $5\frac{1}{4}$ inch diameter, 3/8 inch thick flange joined to it at the other end. This flange had six 1/2 inch holes 3/4 inch from its outside perimeter spaced symmetrically around it. A 3/4 inch thick cover plate was joined to the flange by means of six 1/2 inch bolts and nuts. A 3/8 inch thick rubber gasket with a $1\frac{1}{2}$ inch diameter circle removed from its center sealed the space between the cover plate and flange when they were joined. A 1/8 inch

steel pipe was brought from the top of the bomb through the cover plate to a tee. One side of the tee led to the vacuum pump through a 1/8 inch needle valve; the other side led to one arm of a mercury filled manometer which had a range of 100 centimeters. The other arm of the manometer was opened to the atmosphere. All of the above joints were sealed with either glyptol or shellac. A Sargent Cone-Drive Stirring motor which was operated by 115 volt alternating current was used to operate an eleven inch vertical stirrer which had a two inch diameter burr on its end. A 115 volt precision temperature regulator, manufactured by the Eastern Engineering Company, New Haven, Connecticut, kept a resistance heater and, hence, the water bath at constant temperature. A thermometer which had a range of 0° to 110° C. was sealed through the cover plate into the bomb in a manner such that it could be read down to 10° C.

Molecular Weight (Refer to Figure 2)

The purified cottonseed oil used for this part was the same as that used for the determination of the vapor pressures. The benzene was manufactured by the Merck and Co., Inc., Rahway, N. J. Since it contained 0.006 percent impurities, it was necessary to purify it by fractional crystallization

before it was used. Undistilled water and ice were used for the freezing mixture.

The standard equipment consisted of a Beckman thermometer of range 0° to 6.3° B, a 300 ml. test tube, a one-liter Dewar flask, a size 5 cork stopper and a size 12 rubber stopper. A one-eighth inch glass rod 15 inches long was used for a stirrer. A one inch diameter circle was turned on one end and bent perpendicular to the length of the rod. A wooden support held the Dewar flask which held the 300 ml. test tube and other equipment.

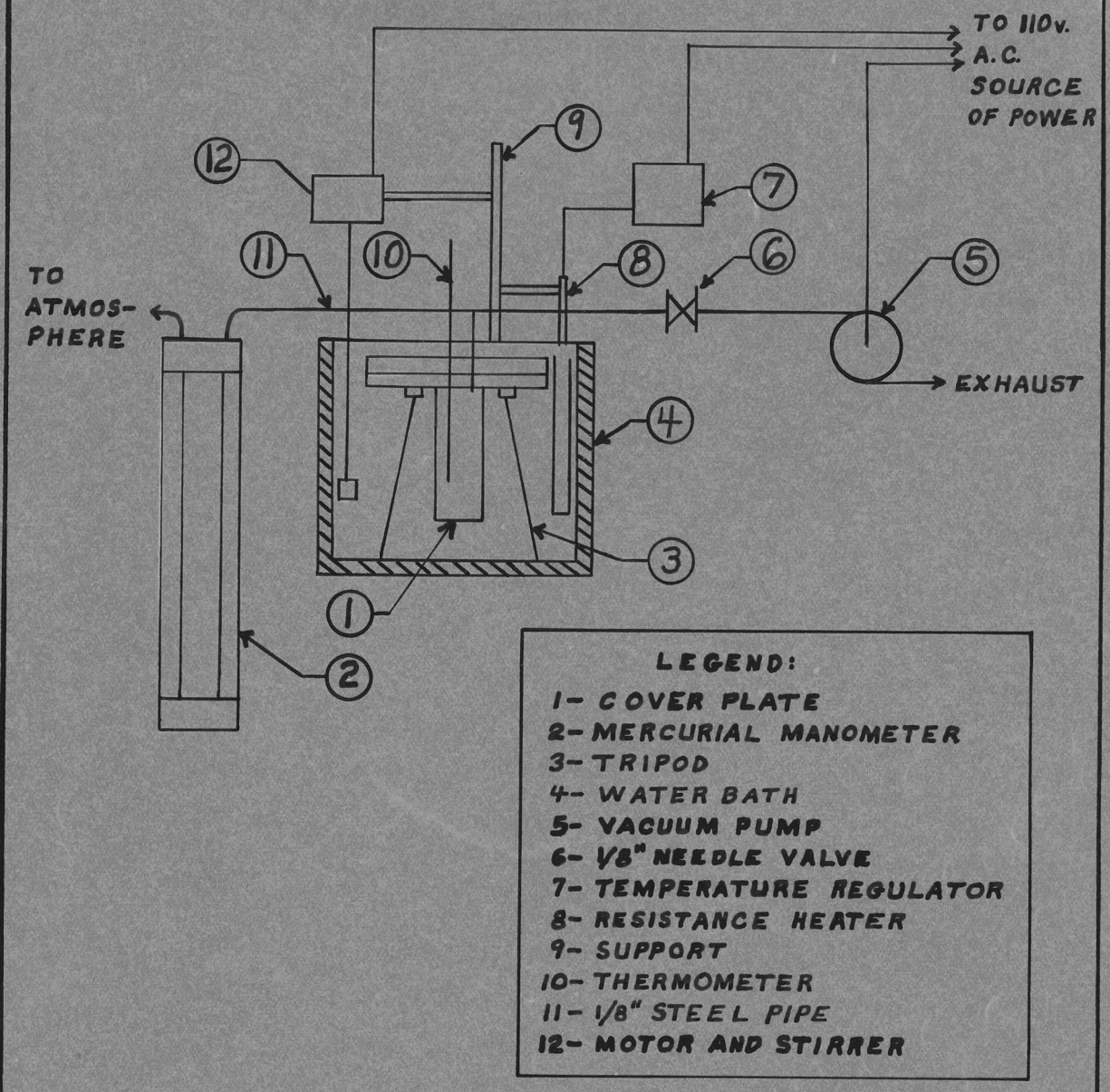

FIG. 1

SCHEMATIC DIAGRAM OF THE EQUIPMENT USED IN THE VAPOR PRESSURE DETERMINATIONS

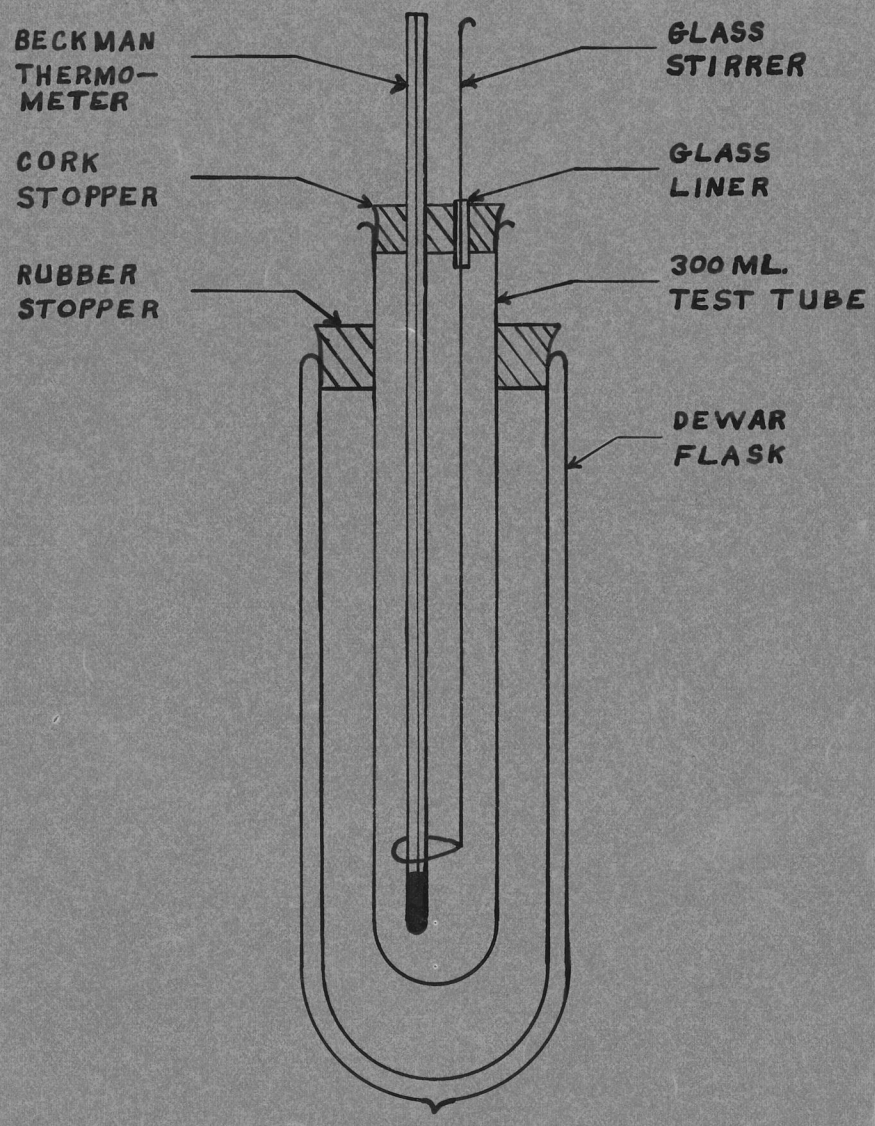

FIG. 2

DIAGRAM OF THE EQUIPMENT USED IN THE COTTONSEED OIL MOLECULAR WEIGHT DETERMINATION

PROCEDURE

Surface Tension

Before any experimental measurements were made, the refractometer and tensiometer were calibrated. Reference is made for the calibrations of the instruments (1, 2).

Twelve samples weighing about ten grams each were used to determine the concentration refractive index relationship of ethyl acetate - cottonseed oil solutions. Ethyl acetate in increments of about 0.1 weight fraction from 0.0 to 1.0 weight fractions were determined with the accuracy of $\pm$ 0.0001 weight fraction on a chain-o-matic balance.

The water bath connections to the refractometer were made, and the temperature was allowed to come to equilibrium at 25° C. Refractive index measurements of the sample were then made with an accuracy of $\pm$ 0.0001 units based on air. Great care was given to the cleanliness of the sample chamber of the instrument and to the length of time the sample was exposed to the open air. Both had great effect on the accuracy of the readings. Reference is made in the literature for the operation of the refractometer. (1)

Eleven samples weighing about one hundred grams each were used to determine the surface tension - temperature

relationship of ethyl acetate - cottonseed oil solutions. Ethyl acetate in increments of about 0.1 mole fraction from 0.0 to 1.0 mole fractions were used. Surface tension measurements at temperatures from 20° C. to 60° C. in increments of ten degrees were made for each sample. Reference is made in the literature for the operation of the tensiometer (2). The sample was heated to about ten degrees above the desired temperature. About 15 cubic centimeters were then poured from the flask into a Petri cup on the platform of the tensiometer. The surface tension was rapidly taken after which a five cubic centimeter sample was taken from the Petri cup and placed in a labeled vial. The temperature of the solution left in the Petri cup was taken.

The refractive index of each of the sample vials was determined from which concentration of ethyl acetate was calculated.

All solutions of ethyl acetate and cottonseed oil were covered to prevent evaporation of ethyl acetate, and they were kept in a refrigerator for overnight storage.

Vapor Pressure (See Figure 1)

The bomb was thoroughly cleaned and dried before the desired ethyl acetate - cottonseed oil mixture was introduced. After the mixture was placed in the bomb, a rubber gasket was inserted between the bomb flange and the cover plate. This joint was then sealed by six bolts which pulled the flange and plate together, tightly squeezing the gasket between them. This assemblage was placed in a water bath. The two outlets from the bomb were attached and sealed to one arm of the manometer and the vacuum pump, respectively. The other arm of the manometer was opened to the atmosphere.

The system was then evacuated to the pressure corresponding to the vapor pressure of the mixture within it. The line leading to the pump was sealed off and the system was allowed to come to equilibrium with the temperature of the water bath. The vapor pressure and its corresponding temperature were recorded. The temperature of the bath was then increased by approximately ten degrees centigrade; the system again reached equilibrium, and the vapor pressure and corresponding temperature were recorded. Four or more vapor pressures and corresponding temperatures which ranged from 20 to 55 degrees centigrade were obtained for each mixture in this manner.

The vapor pressures and temperatures of seven different mixtures ranging from 1 to 100 percent ethyl acetate were obtained.

Molecular Weight (See Figure 2)

One hundred millileters of pure benzene were placed in a large 300 ml. test tube which was sealed with a rubber stopper. A Beckman thermometer and a glass stirrer were inserted through the stopper into the benzene. The test tube was placed in a Dewar flask which was approximately half full of ice and water. The benzene was stirred constantly and its freezing point was determined on the Beckman thermometer.

The test tube was opened and approximately one gram of cottonseed oil was introduced. The freezing point of this mixture of benzene and oil was determined on the Beckman thermometer. The difference in the freezing points of the benzene and this mixture and the weight of cottonseed oil added were recorded. A second weight of cottonseed oil was added and the freezing point of this mixture was obtained as before. The change in freezing points of the benzene and mixture were again recorded. Various weights of oil up to a total of eleven grams were added to the

original 100 ml. of benzene. Each time the change in freezing points was obtained.

Five different 100 ml. portions of benzene were used.

DISCUSSION OF RESULTS

Surface Tension

One experimental source of error was the inaccuracy of temperature measurements while taking the surface tension of the solution. The surface of the liquid, from which surface tension measurements were made, cooled more rapidly than the interior of the liquid; but the temperature measurements were made, including the temperature of the liquid interior. The error was kept within $\pm$ 5° C. for most readings. Another source of error involved the rapid evaporation of ethyl acetate from the solution at temperatures above 30° C. This involved the changing of concentrations of as much as 0.10 weight fraction ethyl acetate at 50° C. The rapidity of measurements determined the size of this error.

The refractive index - concentration relationship of ethyl acetate - cottonseed oil solution for 25° C. is shown in Figure 3. The equation for the resulting straight line was obtained by the method of "least squares" and is as follows:

$$Y = -9.755 \times 10^{-4} + 1.4705$$

Y = refractive index, units based on air

X = concentration of ethyl acetate in weight percent.

The surface tension - temperature relationship for the solutions of different concentrations are shown in Figure 8. Lines were drawn through the points of approximately equal concentrations. Some points were not considered when the lines were drawn because the concentrations were excessively different. More weight was also given to those points in the lower temperature ranges because of their greater accuracy. The ethyl acetate escaped, thus shifting the composition to a solution having more cottonseed oil.

Figure 9 is a cross-plot of Figure 8 giving the relationship of surface tension and concentration for a given temperature. It is observed that a maximum surface tension occurs for a solution rather than a pure liquid. This maximum occurs at about 0.2 mole fraction.

Vapor Pressure

The experimental sources of error were the failure, or inability, to completely evacuate the closed system, the leakage of the system, and the vapor condensation in the manometer arm included in the closed system. A number of attempts were made to evacuate the system completely before any runs were made. The final trial produced a pressure of 2.5 mm. of Hg. within the system at 25° C. At any other temperature the pressure within the system due to incomplete evacuating was calculated with the ideal gas law. The volume and the moles of air within the unfilled system were constant; hence, the pressure at any other temperature could be calculated by $P_2 \times T_2/T_1$. After 2.5 mm. of Hg. was obtained the system was allowed to stand for approximately twenty hours; the rate of leakage was 0.05 mm. of Hg. per hour. No serious trouble was encountered with vapor condensation until the concentration of ethyl acetate in the original sample reached 24.2 percent by weight. For all concentrations of ethyl acetate above this, it was found necessary to heat the manometer arm and the pipe leading to it from the bomb with two 300 watt incandescent lamps.

The original data are recorded in Table 1. The calculated

slopes and intercepts of the curves shown in Figure 4 are recorded in Table II. The 82.0 mm. - 31.0° C. point on the 5.0% curves and the 109.0 mm. - 26.1° C. point on the 60.0% curve were not used in calculating the slope and intercept for their respective curves. There was so much deviation between them and the other points that it was found better not to use them.

Table III is a group of data obtained from Figure 4. It was obtained by specifying a temperature, getting its reciprocal in degrees Kelvin and finding the vapor pressure at each concentration for that temperature. The temperatures 20° to 60° C. were chosen because this is the range to be used in the study of stripping ethyl acetate from cotton-seed oil which is being conducted at the University of Tennessee at the present time. Figure 5 shows these data in graphical form.

Molecular Weight

The source of error was one of lack of precision rather than experimental. The Beckman thermometer used made it possible to read the temperatures to $\pm$ 0.01°, and with the aid of a magnifying glass it was possible to read the temper-

ature to ± 0.002°. This was not sufficiently accurate. For the low weights of oil added, Table IV, the lowering of the freezing point was very small. For this reason an error of ± 0.002° in the temperature would give an error of approximately ± 5.0% in the molecular weight. The laws of colligative properties hold much better at lower concentrations; hence, the smaller weights of oil added gave more accurate results (neglecting the temperature error) than the larger weights, and for this reason the curve in Figure 6 was extrapolated to infinite dilution to obtain the molecular weight of the cottonseed oil. It was determined to be 828.0.

Supercooling of the liquid mixture caused the freezing point to be lowered more than it should have been. This was especially true after the mixture had been frozen and allowed to melt a few times. This source of error was partially overcome by rapid agitation when the freezing point had been passed as the mixture cooled.

TABLE I

CALCULATED DATA FOR THE PLOT COMPOSITION VS.

SURFACE TENSION AT CONSTANT TEMPERATURE

In Figure 9

20° C.		30° C.	
Composition (Mole %)	Surface Tension Dynes/cm.	Composition (Mole %)	Surface Tension Dynes/cm.
100	26.9	100	25.3
88	29.6	89	28.0
79	30.2	79	29.5
64	33.6	70	32.0
57	34.5	57	33.1
50	35.2	53	34.0
38	36.1	38	34.9
30	36.6	30	35.5
0	35.9	0	35.1

TABLE I (Continued)

40° C.		50° C.	
Composition (Mole %)	Surface Tension Dynes/cm.	Composition (Mole %)	Surface Tension Dynes/cm.
100	23.6	100	22.0
88	26.3	87	24.7
75	27.9	77	26.3
66	30.4	66	28.9
55	31.7	55	30.3
50	32.8	50	31.6
38	33.7	38	32.5
30	34.3	30	33.1
0	34.3	0	33.5

60° C.	
Composition (Mole %)	Surface Tension Dynes/cm.
100	20.3
88	22.1
77	24.7
67	27.3
56	28.9
51	30.3
38	31.3
30	31.8
0	32.7

TABLE II

THE CALCULATED SLOPES AND INTERCEPTS

OF THE VAPOR PRESSURE VERSUS RECIPROCAL

OF THE ABSOLUTE TEMPERATURE CURVES

IN FIGURE 4.

Wt. % Ethyl Acetate	Slope A	Intercept B
1.0	-1901.48	7.91374
2.0	-2004.14	8.38045
5.0	-2069.72	8.64041
9.6	-1921.74	8.27837
24.2	-2109.83	8.92094
60.0	-1804.51	8.02083
100.0	-1840.55	8.15675

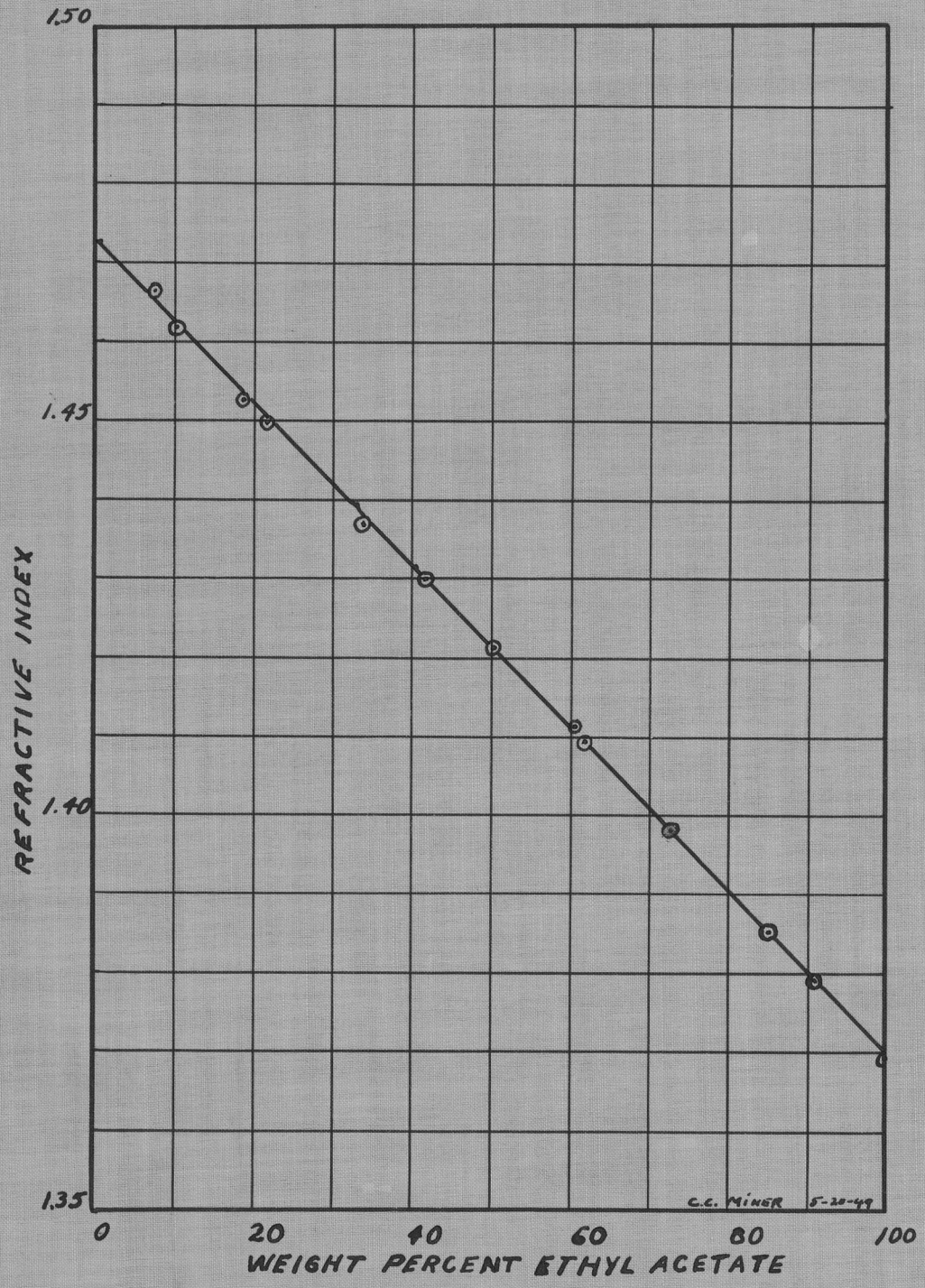

FIGURE 3

REFRACTIVE INDEX VERSUS PERCENT ETHYL ACETATE

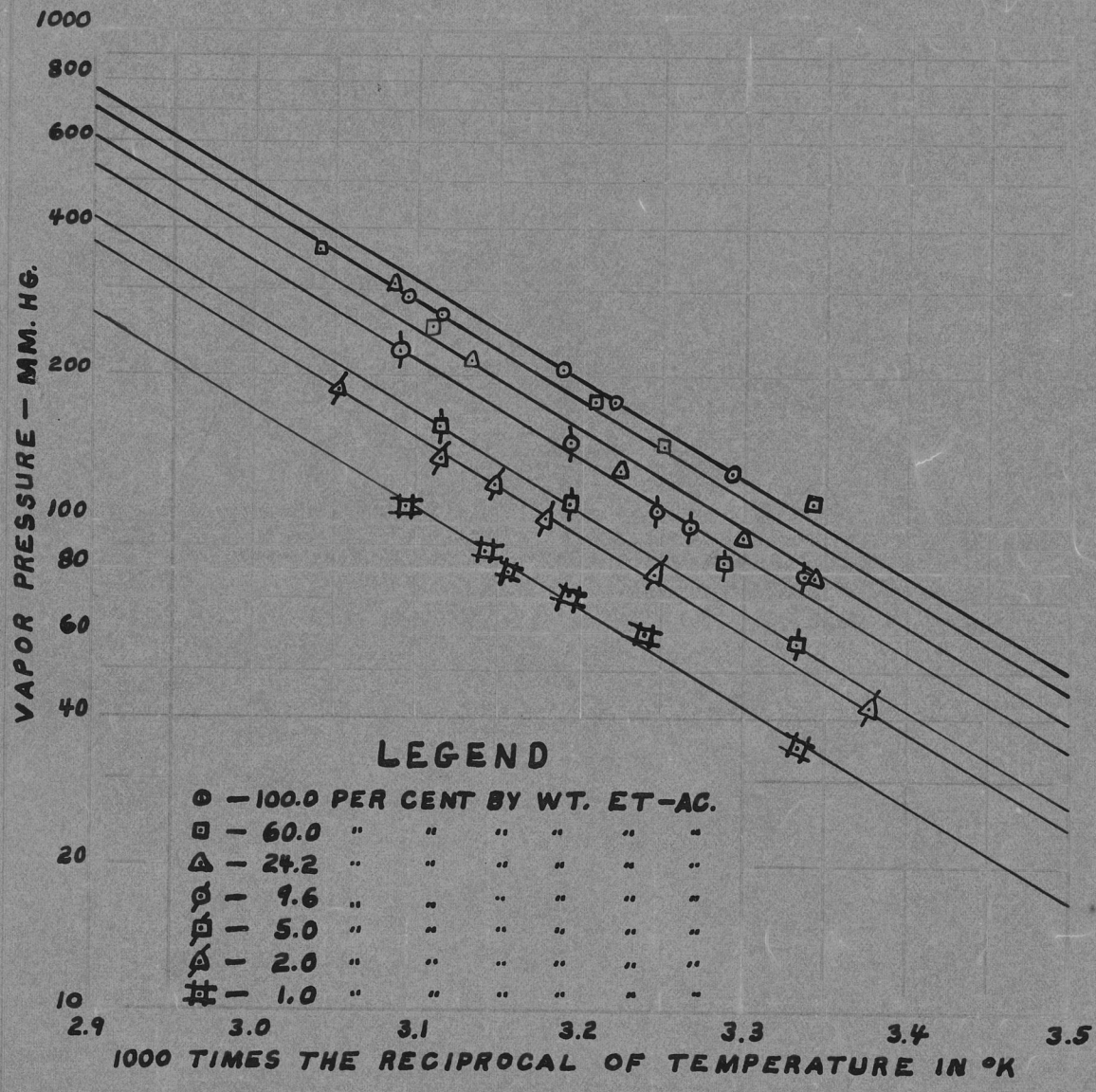

FIG. 4

VAPOR PRESSURE OF COTTONSEED OIL — ETHYL ACETATE MIXTURES PLOTTED AS A FUNCTION OF ABSOLUTE TEMPERATURE

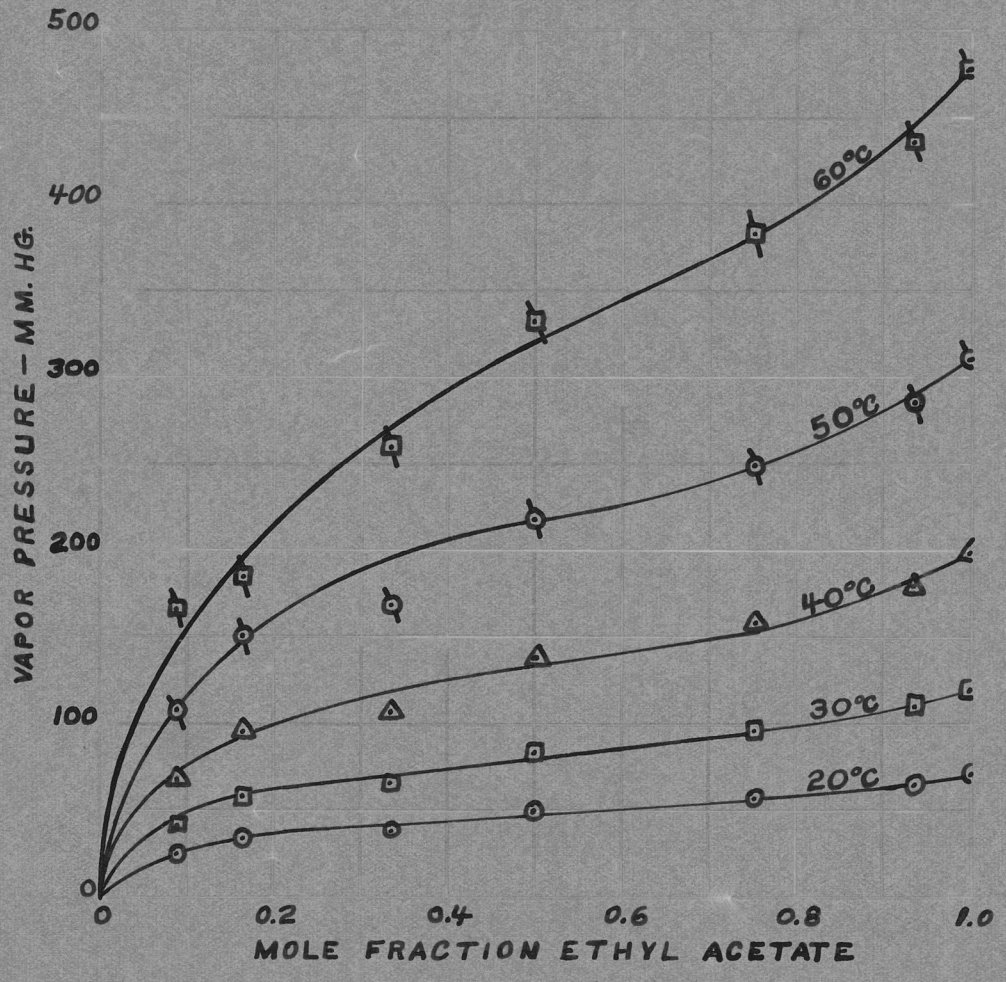

FIG. 5

VAPOR PRESSURE OF COTTONSEED OIL–ETHYL ACETATE MIXTURES PLOTTED AS A FUNCTION OF COMPOSITION AT CONSTANT TEMPERATURE

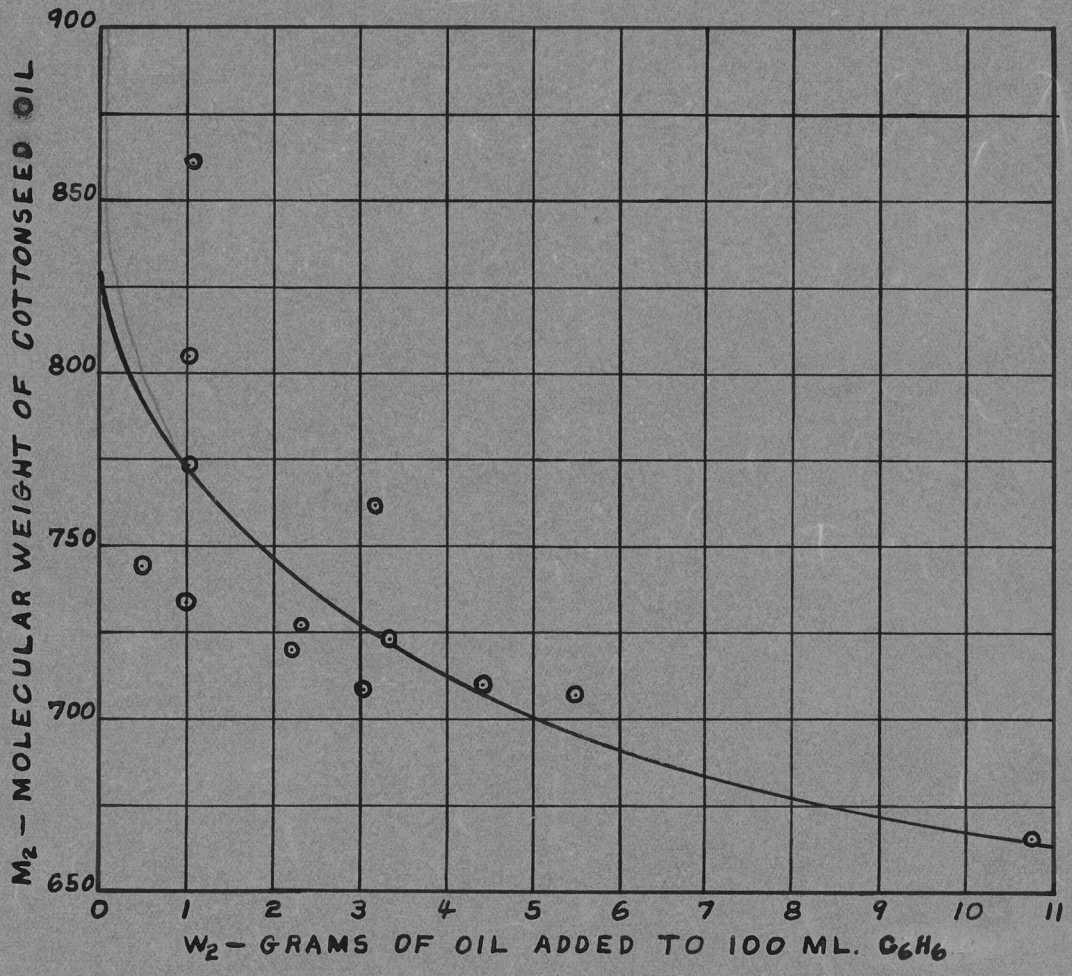

FIG. 6

EXTRAPOLATION OF THE MOLECULAR WEIGHT OF COTTONSEED OIL TO INFINITE DILUTION

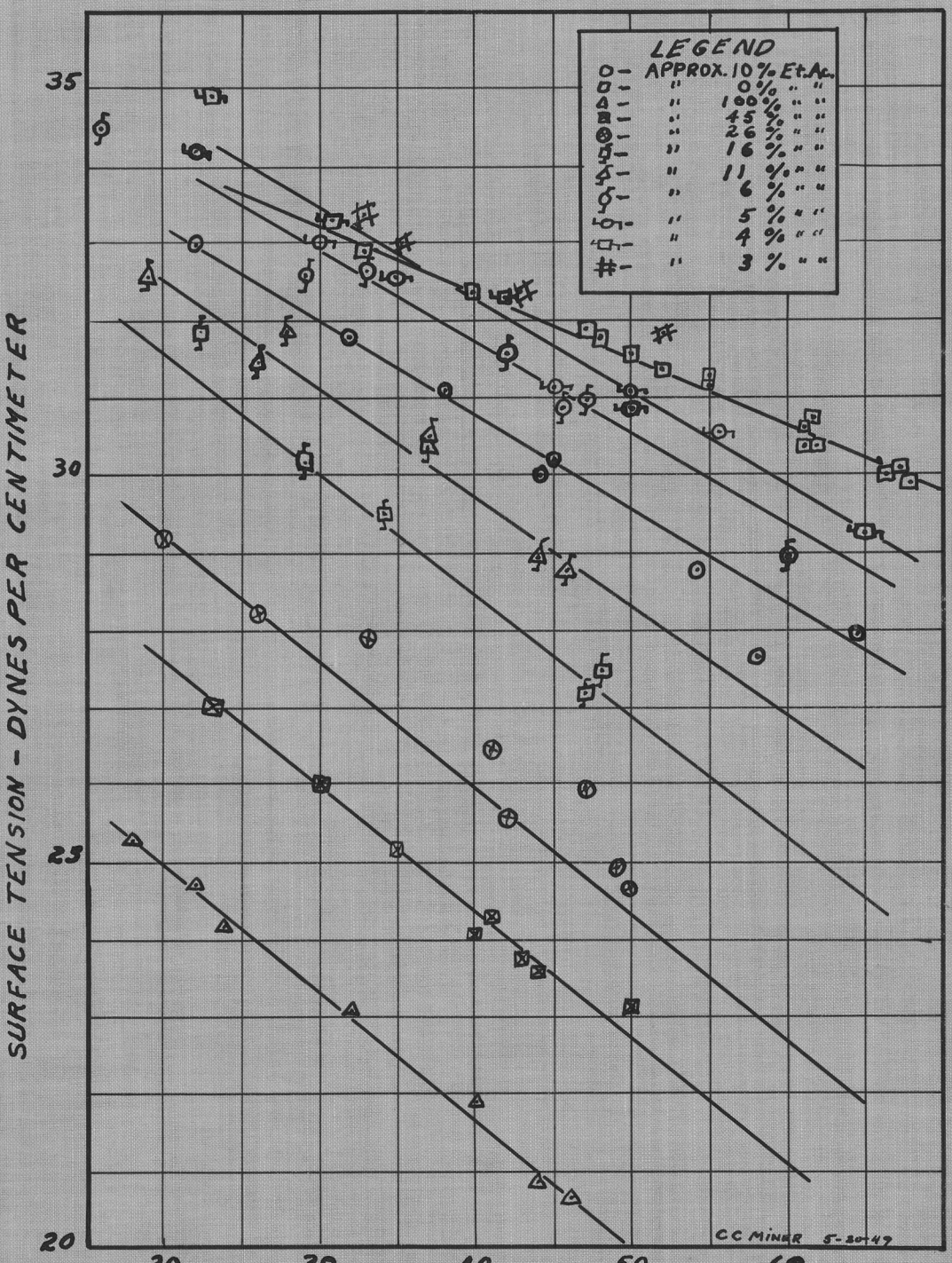

FIGURE 7

SURFACE TENSION VERSUS TEMPERATURE FOR A GIVEN COMPOSITION

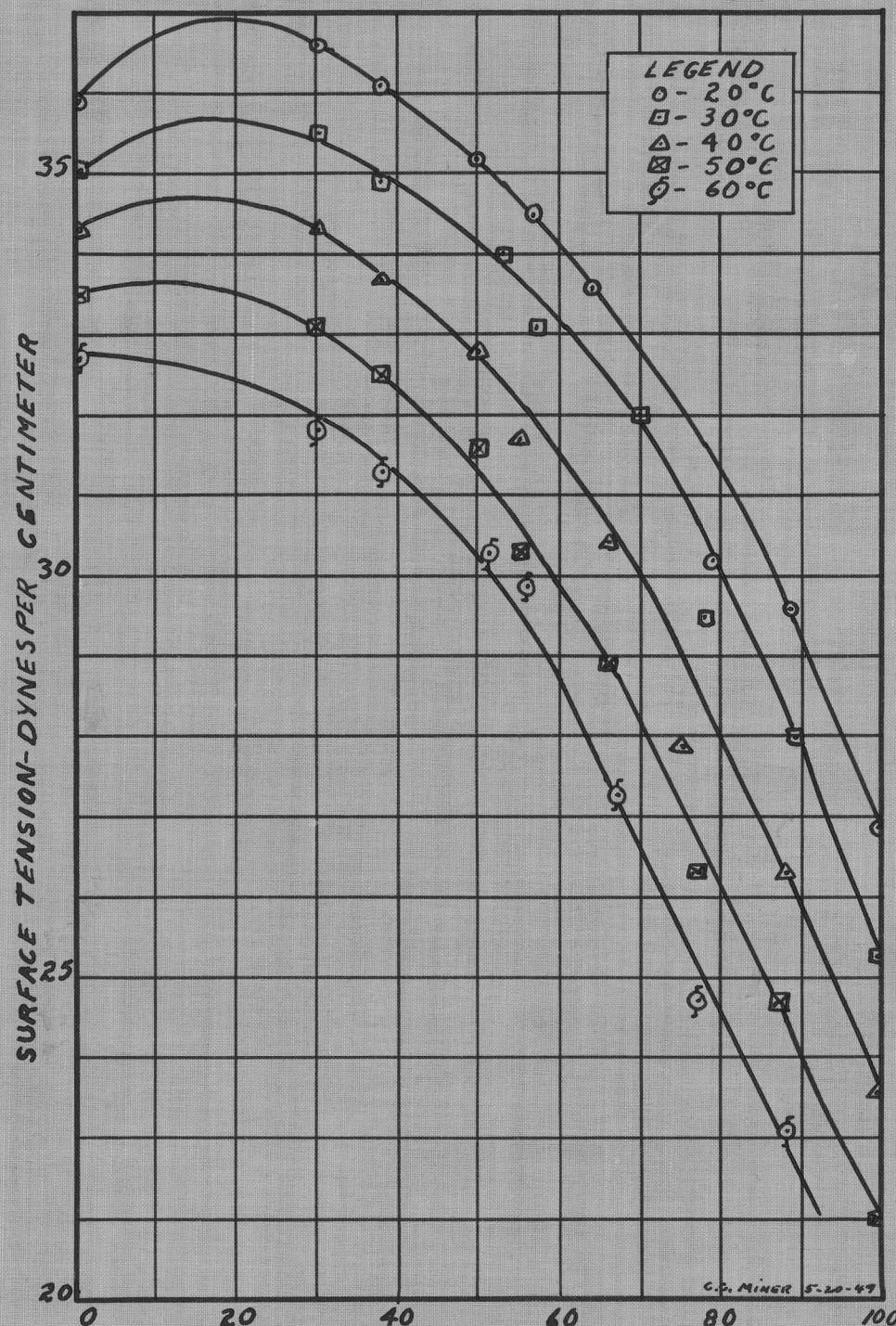

FIGURE 8

SURFACE TENSION VERSUS PER CENT ETHYL ACETATE FOR GIVEN TEMPERATURES

CONCLUSIONS AND RECOMMENDATIONS

Surface Tension

As a result of this investigation, it is concluded that at atmospheric pressure a mixture whose composition is above one percent by weight ethyl acetate of the cottonseed oil - ethyl acetate system will not remain at constant compositions above temperatures of 40° C. The volatile ethyl acetate will vaporize from the mixture.

Due to the change in composition in excess of 40° C., surface tension values were not used in fitting the curves to the data in Figure 7.

It is suggested that more accurate measurements involving better temperature and composition control be taken for this system in order to investigate empirical equations fitting these relationships.

Vapor Pressure

As a result of this investigation it is concluded that vapor pressures of pure liquids or mixtures may be obtained by the method used if some satisfactory method is used to overcome the vapor condensation in the pipe and manometer. It is recommended that any work of this type in the future be performed with a closed system which is entirely

submerged in a constant temperature bath. Since no trouble other than that mentioned was encountered, it is strongly recommended that the advantage of this method, its simplicity, be exploited in the future.

Molecular Weight

Two recommendations are in order here. The first is that a more sensitive thermometer, such as an iron-constantan thermocouple, be used so that the lower concentrations of solute added might be used more than the higher concentrations. The second is that a mechanical agitator of varying speeds be used so that the effects of supercooling be reduced to a minimum.

It is concluded that the molecular weight obtained for the oil is as accurate as the equipment which was available would allow.

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APPENDIX A

Experimental Data

TABLE III-A

DATA FOR THE PLOT OF VAPOR PRESSURE VS. THE RECIPROCAL OF THE ABSOLUTE TEMPERATURE IN FIGURE 4.

Run No.	Wt. Percent Ethyl Acetate	Temperature °C	Vapor Pressure MM. Hg.
1.	1.0	26.5	34.6
	1.0	35.0	59.6
	1.0	40.0	70.6
	1.0	43.6	79.6
	1.0	45.0	87.6
	1.0	50.0	107.0
2.	2.0	23.0	41.7
	2.0	35.0	77.2
	2.0	41.5	100.7
	2.0	44.5	118.7
	2.0	48.0	134.0
	2.0	54.5	185.0
3.	5.0	27.0	56.0
	5.0	31.0	82.0
	5.0	40.0	108.0
	5.0	48.0	156.0
4.	9.6	26.5	77.0
	9.6	33.0	96.5
	9.6	34.8	104.0
	9.6	40.0	144.5
	9.6	50.5	220.0
5.	24.2	26.0	76.0
	24.2	30.0	92.0
	24.2	37.0	126.0
	24.2	46.0	212.0
	24.2	51.0	253.0
6.	60.0	26.1	109.0
	60.0	38.5	175.0
	60.0	48.5	248.0
	60.0	56.0	357.0
	60.0	34.5	141.0
7.	100.0	30.6	124.6
	100.0	37.5	173.6
	100.0	40.5	200.1
	100.0	48.0	260.1
	100.0	50.0	286.1

TABLE III-B

DATA FOR THE PLOT OF VAPOR PRESSURE

VS. COMPOSITION AT CONSTANT TEMPERATURE

In Figure 5.

Mole Fraction Ethyl Acetate	Vapor Pressure - MM. Hg.				
	20°C.	30°C.	40°C.	50°C.	60°C.
1.0000	72.5	121.0	199.0	312.0	478.0
0.9338	66.5	111.0	180.5	286.0	437.0
0.7502	58.0	97.0	159.0	250.0	383.0
0.4998	50.0	84.5	138.0	218.0	333.0
0.3312	38.6	65.3	107.0	169.0	260.0
0.1611	34.8	58.5	96.0	151.0	185.0
0.0867	24.9	42.0	68.5	108.0	166.0

TABLE IV

THE ORIGINAL AND CALCULATED DATA PLOTTED IN FIGURE 6 FOR THE DETERMINATION OF THE MOLECULAR WEIGHT OF COTTONSEED OIL

w_2 - Grams	ΔT_f - °C.	M_2
0.4881	0.038	744.0
0.9881	0.078	733.0
1.0149	0.076	773.0
1.0298	0.074	805.0
1.0716	0.072	861.0
2.2031	0.177	720.0
2.3238	0.185	727.0
3.0520	0.249	708.0
3.1890	0.242	762.0
3.3495	0.268	723.0
4.4094	0.359	710.0
5.4929	0.449	707.0
10.7246	0.931	666.0

TABLE V

DATA FOR THE PLOT OF COMPOSITION

VS. REFRACTIVE INDEX AT CONSTANT TEMPERATURE

In Figure 3 .

Weight percent Ethyl Acetate	Refractive Index		
	Run No. 1	Run No. 2	Run No. 3
4.775	1.4647	1.4664	1.4667
10.017	1.4620	1.4620	-
18.294	1.4528	1.4528	-
33.721	1.4398	1.4372	1.4371
41.519	1.4290	1.4303	1.4302
60.281	1.4152	1.4115	1.4115
61.472	1.4100	1.4091	1.4091
72.247	1.3985	1.3983	-
84.885	1.3850	1.3853	-
90.483	1.3790	1.3791	-
49.989	1.4215	1.4205	1.4213
21.130	1.4499	1.4503	1.4497

TABLE VI

DATA FOR THE PLOT OF SURFACE TENSION VS.

TEMPERATURE AT APPROXIMATELY CONSTANT COMPOSITION

Sample 1

Surface Tension Dynes/cm.	Temperature °C.	Composition Ethyl Acetate (Weight percent)
33.8	32	10.8
33.1	38	10.5
32.2	45	10.0
30.8	54	9.0
32.0	44	7.9
33.0	64	7.3
35.1	22	7.0
35.0	22	7.0

Sample 2

Surface Tension Dynes/cm.	Temperature °C.	Composition Ethyl Acetate (Weight percent)
34.9	33	0
34.8	33	0
34.4	40	0
34.4	41	0
33.8	48	0
33.6	50	0
33.3	55	0

TABLE VI (Continued)

Sample 2 (Continued)

Surface Tension Dynes/cm.	Temperature °C.	Composition Ethyl Acetate (Weight percent)
32.4	61	0
31.9	68	0
33.2	55	0
33.6	50	0
32.4	62	0
32.1	67	0
32.8	59	0
33.4	52	0
30.1	86	0
31.2	75	0
32.0	66	0
32.7	61	0

Sample 3

Surface Tension Dynes/cm.	Temperature °C.	Composition Ethyl Acetate (Weight percent)
25.1	32	100
22.9	44	100
23.9	40	100

TABLE VI (Continued)

Sample 3 (Continued)

Surface Tension Dynes/cm.	Temperature °C.	Composition Ethyl Acetate (Weight percent)
21.2	54	100
22.7	46	100
27.3	18	100
26.7	22	100
26.2	24	100

Sample 4

Surface Tension Dynes / Cm.	Temperature °C.	Composition Ethyl Acetate (Weight percent)
29.1	23	45.0
28.0	30	47.8
27.2	35	47.5
25.6	44	45.2
26.1	40	42.7
26.3	41	42.7
25.8	43	42.7
25.2	50	41.0

TABLE VI (Continued)

Sample 5

Surface Tension Dynes/cm.	Temperature °C.	Composition Ethyl Acetate (Weight percent)
31.2	20	28.8
30.2	26	28.3
29.0	33	27.8
29.0	33	28.0
27.6	42	26.0
27.5	41	23.5
28.0	47	24.8
26.7	50	25.3
27.0	49	24.5

Sample 6

Surface Tension Dynes/cm.	Temperature °C.	Composition Ethyl Acetate (Weight percent)
33.9	23	16.7
32.2	29	19.7
31.5	34	19.6
29.5	48	16.4
29.2	47	15.7
33.5	26	16.1

TABLE VI (Continued)

Sample 7

Surface Tension Dynes/cm.	Temperature °C.	Composition Ethyl Acetate (Weight percent)
33.9	28	12.2
32.5	37	11.0
31.0	44	9.4
30.8	46	11.2
32.4	37	11.8
29.7	58	5.0
34.6	19	12.1

Sample 8

Surface Tension Dynes/cm.	Temperature °C.	Composition Ethyl Acetate (Weight percent)
36.5	21	6.4
34.6	29	7.5
33.6	42	6.2
34.7	33	5.5
32.9	46	5.5
31.0	60	5.2
33.0	47	6.5

TABLE VI (Continued)

Sample 9

Surface Tension Dynes/cm.	Temperature °C.	Composition Ethyl Acetate (Weight percent)
36.2	22	6.1
35.0	30	5.7
34.6	35	6.1
33.2	45	5.0
32.9	50	4.5
32.6	56	5.0

Sample 10

Surface Tension Dynes/cm.	Temperature °C.	Composition Ethyl Acetate (Weight percent)
36.9	23	4.0
35.3	31	3.9
33.1	50	3.8
34.3	42	3.8
31.3	65	3.3

TABLE VI (Continued)

Sample 11

Surface Tension Dynes/cm.	Temperature °C.	Composition Ethyl Acetate (Weight percent)
36.6	22	3.5
35.4	33	3.8
35.0	36	4.5
33.9	52	3.3
34.4	43	4.4
32.1	55	2.5

APPENDIX B

Sample Calculations

SAMPLE CALCULATIONS

Surface Tension:

A. Calculation of the weight fraction of ethyl acetate in an ethyl acetate - cottonseed oil solution. Using sample number one:

Weight of bottle..... = 12.1856 grams.

Weight of bottle + cottonseed oil = 20.0298 grams.

Weight of cottonseed oil .....= 7.8442 grams.

Weight of bottle + cot.seed oil + Ethyl acetate.....= 20.4231 grams.

Weight of ethyl acetate.....= 7.8442 + .3933 +cottonseed oil

= 8.2375 grams.

% Ethyl acetate in solution.....= $100 \times \frac{.3933}{8.2375} = 4.775\%$

B. Conversion of mole fraction to weight fraction.

Using .10 mole fraction ethyl acetate:

x = weight fraction ethyl acetate

827 = molecular weight cottonseed oil

88.10 = molecular weight ethyl acetate

$$0.100 = \frac{\frac{x}{88.10}}{\frac{x}{88.10} + \frac{1.0 - x}{827}}$$

Solving for x = .0117

Vapor Pressure:

The calculation of the slope A and the intercept B, which appear in Table II for all concentrations, is illustrated here with the 1.0% ethyl acetate curve which appears in Figure 4.

V.P. - mm. Hg	T - °C.	T - °K	1/T °K	$(1/T\ ^{\circ}K)^2$
34.6	26.5	299.7	0.003337	1.1133367×10^{-5}
59.6	35.0	308.2	0.003245	1.0527754×10^{-5}
70.6	40.0	313.2	0.003193	1.0194291×10^{-5}
79.6	43.6	316.8	0.003157	0.9963934×10^{-5}
87.6	45.0	318.2	0.003143	0.9876438×10^{-5}
107.0	50.0	323.2	0.003094	0.9573208×10^{-5}
			$\Sigma = 0.019169$	$\Sigma = 6.1268992 \times 10^{-5}$

log P	log P/T
1.53908	0.00513540
1.77525	0.00576006
1.84880	0.00590294
1.90091	0.00600036
1.94250	0.00610466
2.02938	0.00627902
$\Sigma = 11.03592$	$\Sigma = 0.03518224$

The equation of the curves in Figure 4 is:

$$\log P = \frac{A}{T} + B$$

and from the "method of least squares" the equations for solving for the constants A and B are:

$$\Sigma (\log P) = A\Sigma\left(\frac{1}{T}\right) + nB$$

and

$$\Sigma (\log P/T) = A\Sigma\left(\frac{1}{T}\right)^2 + B\Sigma\left(\frac{1}{T}\right)$$

where 'n' is the number of terms making up the sum.

By this method the constants for 1% ethyl acetate were found to be:

$$A = -1901.48 \qquad \text{and} \qquad B = 7.91374$$

Molecular Weight

The equation used for the calculation of the molecular weight is:

$$M = \frac{1000\ K_f}{w_1} \times \frac{w_2}{T_f}$$

where:

M_2 = the molecular weight to be determined.

w_2 = the weight in grams of cottonseed oil added to the solvent, benzene.

T_f = the degrees centigrade by which the oil lowered the freezing point of the benzene.

w_1 = the weight in grams of solvent.

K_f = 5.12, the molal freezing point depression constant of benzene.

When 100.0 ml. of benzene was used as the solvent this equation reduced to:

$$M_2 = 58.248 \times \frac{w_2}{\Delta T_f}$$

The original data, w_2 and ΔT_f, and the molecular weights are recorded in Table IV. The molecular weight is plotted against w_2 in Figure 6. There, the curve was extrapolated to $w_2 = 0$ and the molecular weight of cottonseed oil was found to be 828.0.

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APPROVAL

The foregoing thesis is hereby approved as a creditable study of an engineering subject carried out and presented in a manner sufficiently satisfactory to warrant its acceptance as a prerequisite to the degree for which it has been submitted. It is to be understood that by this approval the undersigned does not necessarily endorse or approve any statement made, opinions expressed, or conclusions drawn therein, but approves the thesis only for the purpose for which it is submitted.

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