THE EFFECT OF DIMETHYLANILINE ADDITION ON THE SEPARATION OF ACETIC ACID AND WATER BY DISTILLATION

By

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF FIGURES (Cont.)

SUMMARY

The effect of dimethylaniline addition on the vapor-liquid equilibrium of the system acetic acid-water was investigated. The complete range of acetic acid-water ratios was covered; dimethylaniline percentages in the liquid phase ranged from zero to ninety weight percent. Separation was increased with the addition of dimethylaniline, the greatest increase in separation taking place in the acetic acid-rich region. Also investigated was the vapor-liquid equilibrium of the system acetic acid-dimethylaniline and the liquid-liquid equilibrium at 25°C. of the ternary system, acetic acid-dimethylaniline-water.

A method of analysis for the ternary system, based upon refractive index and acetic acid titration, was developed and successfully used.

A schematic flow diagram for a proposed separation of acetic acid and water by extractive distillation with dimethylaniline is presented.

INTRODUCTION

A large percentage of the acetic acid used commercially at the present time is recovered from pyroligneous liquors obtained from the destructive distillation of hardwood wastes. The acid, as such, is in a dilute solution and must be separated from a large quantity of water. Due to the low relative volatility of this system in the water-rich region, distillation is expensive because of the large number of plates required. Attempts have been made to improve the relative volatility of this system by the addition of a third component[17,10]. These methods are summarized:

1. Countercurrent extraction of the acid with a light solvent such as ether, chloroform, or acetone will yield about 70-90% acid. Benzene or petroleum ether will yield about 90-99% acid.

2. Extractive distillation with a heavy solvent such as dibutyl phthallate, diethyl phthallate, and methyl cyclohexanone has been employed.

3. Separation by forming a complex with an organic base such as quinoline or quinolidine, which complex can then be broken up after separation, finds some application.

4. Extraction with an organic solvent, followed by salting out, has been utilized in some cases.

5. Fixation of the water by hygroscopic agents is used extensively in the final concentration step. Suggested agents for this purpose are $CaCl_2$, Na_2SO_4, $CuSO_4$, and H_3PO_4,

6. Distillation in the presence of a fixating agent such as anhydrous sodium acetate will give around 80% recovery of the acid at a concentration of 98.6%. The recovery by this operation is increased by reducing the pressure.

7. Distillation with a liquid such as xylene, benzene or ethyl acetate which will form a minimum-boiling azeotrope with water, finds widespread use today.

8. Reversal of the relative volatility with removal of the acetic acid in the overhead has been accomplished on an experimental basis by distillation in the presence of calcium chloride.

It was felt that the addition of an organic nitrogen compound to the acetic acid-water system might increase the relative volatility of water to acetic acid. This third component must not form an azeotrope with acetic acid. Its boiling point should be sufficiently high so that its separation from acetic acid would not be difficult, and yet not so high as to require extremely high pressure steam for vaporization and large amounts of steam to meet sensible heat requirements.

At first, aniline was investigated because it seemed to posses the necessary properties, but it was subsequently abandoned due to the reaction between aniline and acetic acid to form acetanilide. A method of analysis for aniline, developed during this part of the investigation, appears in the appendix. Dimethylaniline, with no active hydrogens attached to the nitrogen atom, was then selected as the added component to be investigated.

STATEMENT OF THE PROBLEM

Since data are available only for the system acetic acid-water, to work dealt with the following phases of investigation:

1. Development of an analytical method for determination of dimethylaniline.

2. Determination of vapor-liquid equilibrium data for the system acetic acid-water and comparison of experimental values with values found in the literature.

3. Determination of vapor-liquid equilibrium data for the system acetic acid-dimethylaniline.

4. Determination of vapor-liquid equilibrium data for the system water-acetic acid-dimethylaniline.

MATERIALS USED

1. Distilled water was used throughout the investigation.

2. Acetic acid: Acetic acid of C. P. grade and assaying 99.5% acetic acid by weight was obtained from the J. T. Baker Chemical Co. For the determination of the acetic acid-dimethylaniline vapor-liquid equilibrium, and for the determination of refractive indices of acetic acid-dimethylaniline mixtures, a more concentrated acid was desired. An assay of 99.8% was obtained on material prepared by the following method: Anhydrous sodium sulphate was dried at 120°C. for 12 hours. The sodium sulphate and acetic acid were placed in a tightly stoppered bottle, shaken well, and allowed to stand for 24 hours. The acetic acid layer was decanted into a flask and distilled in a three-ball Snyder column. Only the fraction boiling between 240-243°F. was used.

3. Dimethylaniline: Dimethylaniline (free from mono), B. P. 192-193°C., was obtained from The Matheson Co. Inc. (chemical no. 5053). It was used directly. During the latter part of the investigation it was necessary to recover the dimethylaniline for further use. The dimethylaniline was present in solution with water and acetic acid. The solution was reacted with sodium carbonate until it was basic to phenolphthalein. The dimethylaniline layer, which separated from the rest of the solution, was removed. It was then washed with water and steam distilled. Purity of the recovered dimethylaniline was checked against that of the original by refractive index. It was also checked for the presence of acetic acid by titration with standard base. No acetic acid was found.

INSTRUMENT USED

For refractive index determinations, an Abbe refractometer was used. The temperature was controlled by means of a constant-temperature bath and a circulating pump. The refractometer was adjusted to read correctly by checking with water and with a standard glass prism.

PROCEDURE

Solubility Envelope:

The solubility envelope at 25°C. for the ternary system water-acetic acid-dimethylaniline was determined by the cloud point method, using burettes with which volumes could be estimated to a thousandth of a ml. The samples were run from clear to cloud; they were then cleared with a fraction of a drop. The readings on the burettes were recorded, room temperature was recorded, and refractive indices were taken on the clear samples. The composition of samples was determined by conversion of the volumes of the pure components to weights by density tables[1,2,3,4]. The results thus obtained are represented by Table I, Fig. 1, and the solubility envelope of Fig. 2. Conjugate layer compositions at 25°C. for the system water-acetic acid-dimethylaniline appear in Table II. These data were obtained by titration of the conjugate phases for acetic acid content. It is apparent that liquid-liquid extraction of acetic acid with dimethylaniline at 25°C. is not feasible.

Analytical Technique:

Attempts were made to analyze dimethylaniline by bromination,[11,12] but the results were too erratic. The physical properties of water, acetic acid, and dimethylaniline were investigated in order that some physical differences might be used as a means of analysis. Refractive index seemed to present the best method of analysis, so this property was used. Refractive indices were determined at 25°C. for known synthetic solutions of acetic acid-water, acetic acid-dimethylaniline, and for acetic acid-water-dimethylaniline in the single phase region.

The results are presented in Table II and Figure 2. Refractive indices of the acetic acid-water system are compared with literature values[5] in Table IV. The refractive index of dimethylaniline at 25°C., calculated from the literature value at 20°C. (1.5587) and the molar refraction equation, is 1.5558. The experimental value of 1.5560 compares favorably with this.

The individual systems were analyzed as follows:

<u>Acetic acid-water</u>: Approximately five ml. of sample were weighed, diluted to 250 ml. and a convenient aliquot taken for acetic acid titration with approximately 0.1N standard NaOH. The caustic was standardized against potassium acid phthalate, with phenolphthalein as the indicator. The aliquot titrations were made in duplicate; these checked on the average to 0.02 ml. Water was determined by difference.

<u>Acetic acid-dimethylaniline</u>: This system was analyzed by taking the refractive index of the sample and referring to the calibration curve (fig.2). The values were occasionally spot-checked by acetic acid titration and found to be consistent. The titration of acetic acid is not affected by the presence of dimethylaniline. This was proved by titration of known synthetic mixtures of the two components.

<u>Acetic acid-water-dimethylaniline</u>: This system was analyzed by one of two methods, depending upon the number of phases present in the sample. The single phase samples were analyzed by refractive index and by titration of an aliquot with approximately 0.1N NaOH. The calibration curve (Fig. 2) was used to read off the

dimethylaniline concentration. Water was determined by difference. Two-phase samples were collected in centrifuge tubes, which were then placed in a constant temperature bath at 25°C. The tubes were shaken frequently over a two-hour period and each phase was withdrawn with a capillary pipette. Each phase was weighed separately and titrated for acetic acid. The knowledge of the acetic acid concentration in each layer permitted the location of the conjugate points on the triangular-plot solubility envelope; these points were joined by a tie line. The lever arm principle was used to locate the bulk concentration of the original sample.

TABLE I

MUTUAL SOLUBILITY OF THE SYSTEM WATER-ACETIC ACID-DIMETHYLANILINE AT 25°C; CLOUD POINT METHOD PERCENTAGE BY WEIGHT

Experimental Data

n_D^{25}	%HAc	%H_2O	%DMA
1.5384	9.5	1.1	89.4
1.5191	19.6	1.6	78.8
1.5136	22.8	2.8	74.4
1.5120	23.6	2.3	74.1
1.5073	25.8	3.1	71.1
1.4750	36.4	6.4	57.2
1.4705	41.6	7.7	50.7
———	42.1	8.5	49.4
1.4604	45.9	9.6	44.5
1.4613	45.8	9.8	44.4
1.4766	45.9	10.3	43.8
1.4520	47.7	12.1	40.2
1.4440	49.0	13.5	37.5
1.4394	50.0	16.3	33.7
1.4375	50.5	16.7	32.8
1.4335	50.4	18.9	30.7
1.4315	50.2	19.3	30.5
1.4257	50.0	22.5	27.5
1.4131	47.1	30.6	22.3
1.4095	45.8	33.2	21.0
1.4024	43.2	38.7	18.1
1.3951	39.3	44.7	16.0
1.3913	37.5	47.6	14.9
1.3853	34.1	52.5	13.4
1.3790	30.4	57.8	11.8
1.3767	30.3	59.5	10.2
1.3738	27.4	62.1	10.5
1.3675	23.2	67.6	9.2
1.3595	18.4	74.2	7.2
1.3536	14.7	80.2	5.1
1.3525	13.8	80.9	5.3
1.3455	8.5	87.7	3.8
1.3450	8.2	87.6	4.2
1.3436	8.5	88.4	3.1
1.3387	2.2	93.2	4.6
1.3385	3.7	93.4	2.9
1.3384	3.6	94.3	2.1

Smoothed Data

n_D^{25}	%HAc	%H_2O	%DMA
* 1.5560	0.0	0.0	100.0
1.5465	5.0	0.7	94.3
1.5370	10.0	0.9	89.1
1.5275	15.0	1.5	83.5
1.5180	20.0	2.2	77.8
1.5085	25.0	2.8	72.2
1.4985	30.0	3.7	66.3
1.4887	35.0	4.8	60.2
1.4765	40.0	6.6	53.4
1.4625	45.0	9.5	45.5
1.4560	47.0	11.2	41.8
1.4474	49.0	13.4	37.6
1.4440	50.0	15.1	34.9
1.4360	50.3	18.5	31.2
1.4332	50.0	21.5	28.5
1.4223	49.0	25.5	25.5
1.4130	47.0	31.2	21.8
1.4080	45.0	35.4	19.6
1.3974	40.0	43.9	16.1
1.3878	35.0	51.4	13.6
1.3788	30.0	58.5	11.5
1.3704	25.0	65.3	9.7
1.3625	20.0	72.2	7.8
1.3550	15.0	79.0	6.0
1.3479	10.0	85.8	4.2
1.3406	5.0	92.8	2.2
** ———	0.0	100.0	0.0

* The refractive index of dimethylaniline saturated with water is the same as that of pure dimethylaniline.

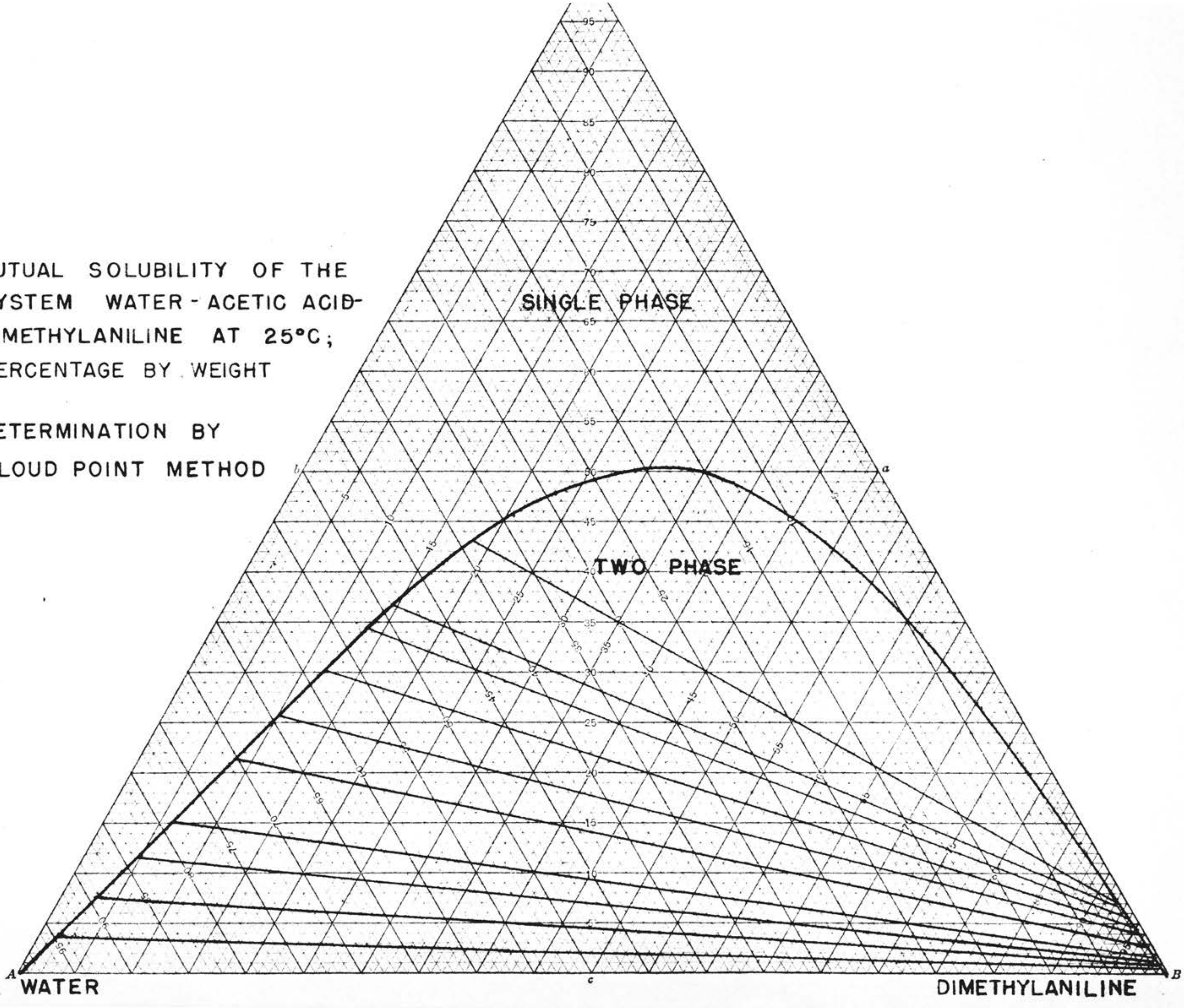
** Dimethylaniline was found to be soluble in water (by titration) to less than 0.1%.

TABLE II

CONJUGATE LAYER COMPOSITIONS IN THE SYSTEM WATER-ACETIC ACID-DIMETHYLANILINE AT 25°C.

Wt. % HAc in Water Phase	Wt. % HAc in DMA Phase
3.5	0.47
3.9 *	0.36 *
6.3	0.55
7.7 *	0.77 *
8.6	0.86
11.1	1.3
11.6 *	1.4 *
12.8	1.6
14.0	1.6
15.1 *	1.7 *
16.2	1.9
18.0	2.1
18.3	2.8
20.6	3.2
21.4 *	2.7 *
22.9	3.5
24.0	3.3
25.7 *	4.1 *
26.3	4.2
28.0	4.5
28.2	4.5
29.5	5.3
30.1 *	4.7 *
32.2	5.2
33.1	5.5
34.3 *	5.5 *
36.8 *	6.4 *
43.1 *	6.8 *

* Indicates data used in construction of tie lines for Fig. 1.



MUTUAL SOLUBILITY OF THE SYSTEM WATER-ACETIC ACID-DIMETHYLANILINE AT 25°C; PERCENTAGE BY WEIGHT

DETERMINATION BY CLOUD POINT METHOD

FIG. 1

TABLE III

SYSTEM: WATER-ACETIC ACID-DIMETHYLANILINE
REFRACTIVE INDICES AT 25°C.
PERCENTAGE BY WEIGHT

Experimental Data				Smoothed Data			
N_D^{25}	%HAc	%H_2O	%DMA	n_D^{25}	%HAc	%H_2O	%DMA
System: Acetic acid-Dimethylaniline							
1.3965	90.0		10.0	1.3691	100.0		0.0
1.4186	80.0		20.0	1.3965	90.0		10.0
1.4374	70.0		30.0	1.4185	80.0		20.0
1.4551	60.0		40.0	1.4375	70.0		30.0
1.4715	50.0		50.0	1.4550	60.0		40.0
1.4870	40.0		60.0	1.4712	50.0		50.0
1.5041	30.0		70.0	1.4875	40.0		60.0
1.5204	20.0		80.0	1.5035	30.0		70.0
1.5385	10.0		90.0	1.5203	20.0		80.0
1.5560	0.0		100.0	1.5382	10.0		90.0
				1.5560	0.0		100.0
System: Acetic Acid-Water							
1.3325	0.0	100.0		1.3325	0.0	100.0	
1.3395	10.0	90.0		1.3395	10.0	90.0	
1.3462	20.0	80.0		1.3462	20.0	80.0	
1.3529	30.0	70.0		1.3528	30.0	70.0	
1.3585	40.0	60.0		1.3588	40.0	60.0	
1.3640	50.0	50.0		1.3640	50.0	50.0	
1.3685	60.0	40.0		1.3686	60.0	40.0	
1.3725	70.0	30.0		1.3724	70.0	30.0	
1.3536	75.0	25.0		1.3750	80.0	20.0	
1.3750	80.0	20.0		1.3755	85.0	15.0	
1.3754	85.0	15.0		1.3756	90.0	10.0	
1.3755	90.0	10.0		1.3745	95.0	5.0	
1.3745	95.0	5.0		1.3691	100.0	0.0	
1.3698	99.8	0.2					
System: Acetic Acid-Water-Dimethylaniline							
1.3766	30.0	60.0	10.0	1.3771	30.0	60.0	10.0
1.3826	40.0	50.0	10.0	1.3822	40.0	50.0	10.0
1.3875	50.0	40.0	10.0	1.3876	50.0	40.0	10.0
1.3919	60.0	30.0	10.0	1.3930	60.0	30.0	10.0
1.3973	70.0	20.0	10.0	1.3968	70.0	20.0	10.0
1.3976	80.0	10.0	10.0	1.3983	80.0	10.0	10.0
				1.3965	90.0	0.0	10.0

TABLE III (cont.)

Experimental Data				Smoothed Data			
n_D^{25}	%HAc	%H_2O	%DMA	n_D^{25}	%HAc	%H_2O	%DMA
System: Acetic Acid-Water-Dimethylaniline (cont.)							
1.4105	50.0	30.0	20.0	1.4107	50.0	30.0	20.0
1.4154	60.0	20.0	20.0	1.4155	60.0	20.0	20.0
1.4193	70.0	10.0	20.0	1.4190	70.0	10.0	20.0
1.4186	80.0	0.0	20.0	1.4192	75.0	5.0	20.0
				1.4185	80.0	0.0	20.0
1.4225	50.0	25.0	25.0	1.4225	50.0	25.0	25.0
1.4256	60.0	15.0	25.0	1.4253	55.0	20.0	25.0
1.4285	65.0	10.0	25.0	1.4276	60.0	15.0	25.0
1.4286	70.0	5.0	25.0	1.4285	65.0	10.0	25.0
				1.4290	70.0	5.0	25.0
				1.4280	75.0	0.0	25.0
1.4354	55.0	15.0	30.0	1.4356	55.0	15.0	30.0
1.4376	60.0	10.0	30.0	1.4370	60.0	10.0	30.0
1.4376	65.0	5.0	30.0	1.4377	65.0	5.0	30.0
				1.4375	70.0	0.0	30.0
1.4445	51.0	14.0	35.0	1.4445	50.0	15.0	35.0
1.4446	54.0	11.0	35.0	1.4447	55.0	10.0	35.0
1.4456	60.4	4.6	35.0	1.4451	60.0	5.0	35.0
				1.4465	65.0	0.0	35.0

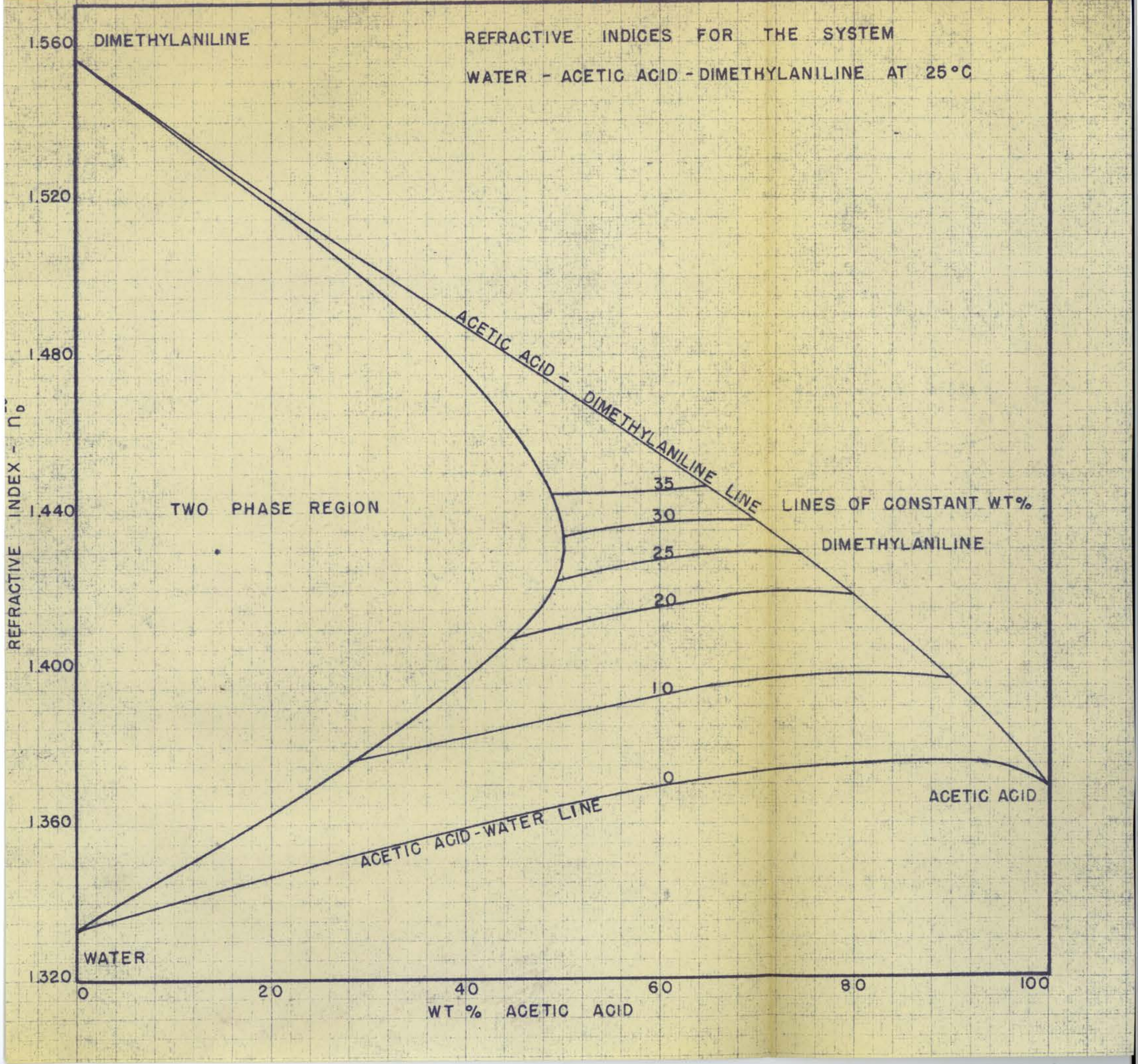
TABLE IV

SYSTEM: WATER-ACETIC ACID
REFRACTIVE INDICES AT 25°C.
EXPERIMENTAL VERSUS LITERATURE VALUES

	n_D^{25}			n_D^{25}	
Wt. % HAc	Exp.	Lit.	Wt. % HAc	Exp.	Lit.
0.0	1.3325	1.3325	18.0	1.3450	1.3449
2.5	1.3343	1.3343	19.3	1.3458	1.3458
4.5	1.3358	1.3357	21.1	1.3470	1.3470
6.7	1.3373	1.3372	23.3	1.3485	1.3484
8.5	1.3386	1.3385	25.0	1.3496	1.3495
10.7	1,3400	1,3400	26.9	1,3508	1.3507
13.2	1.3417	1,3417	28.8	1,3520	1,3519
15.2	1,3432	1,3431	29.0	1,3523	1,3523

Note: No literature values were available for higher concentrations.

FIG. 2


REFRACTIVE INDICES FOR THE SYSTEM
WATER - ACETIC ACID - DIMETHYLANILINE AT 25°C
DIMETHYLANILINE
WATER
ACETIC ACID
TWO PHASE REGION
ACETIC ACID - DIMETHYLANILINE LINE
ACETIC ACID-WATER LINE
LINES OF CONSTANT WT%
DIMETHYLANILINE
35
30
25
20
10
0
1.560
1.520
1.480
1.440
1.400
1.360
1.320
REFRACTIVE INDEX - n_D
0
20
40
60
80
100
WT % ACETIC ACID

Operational Technique:

Vapor-Liquid Equilibrium

For the two component system runs and the single liquid phase (both distillate and residue) runs for the three component systems, the Othmer still[6] was used. A recently developed two-phase still by Hands and Norman[7] was used for the three component system for all the two-phase runs and part of the single-phase runs for this system. Pressure on the still was maintained at 760 ± 1 mm. of mercury by means of a Model No. 5 Industrial Cartesian Manostat, available through the Emil Greiner Company, New York City. The pressure source used to operate the manostat was compressed air. The thermometers used in this investigation were calibrated in place by checking with distilled water (boiling point 100.0°C.) and with dimethylaniline (boiling point 193.0°C.). Temperatures were estimated to 0.1°C. The neoprene stoppers which held the thermometers in place showed some tendency to swell during operation.

Othmer Still: (Fig.3)

The charge to the Othmer still was about 450 ml. The still was run for forty-five minutes at a rate of 60-65 drops of distillate per minute, the temperature was recorded, and distillate and residue samples of about 5 ml. were withdrawn for analysis. Equilibrium was reached in forty-five minutes. This was proved by withdrawing a small sample of distillate after forty-five minutes and another sample after two hours. Comparison of the analysis of these two samples showed them to be the same. Changes in the still-pot composition from run to run were made by withdrawing part of the charge and replacing with one of the pure components.

Hands and Norman Still: (Fig.4)

The initial charge to the Hands and Norman still was about 350 ml. The still was run for about forty minutes, although constancy of temperature was obtained after twenty minutes. After forty minutes of operation, the temperature was recorded, the stopcock turned to mid-position, and a sample (1-5 ml.) allowed to collect in the distillate chamber. The stopcock was then turned so that the sample ran into the sample bottle. It was then turned back to its original position and the temperature again recorded after it became constant. The composition of the still pot was changed by the addition of pure components. Since nothing was removed from the still other than the distillate sample, the still-pot charge was larger after each run and varied from 350-800 ml. Because the Hands and Norman still gives an average result, an effort was made to keep the size of the distillate sample small relative to the still pot charge (one percent or less).

Because of the slight pressure in the still relative to the atmosphere (the average atmospheric pressure was 740 mm.), the stopcock was always blown clean when samples were collected. Any liquid clinging to the walls of the sampling outlet was removed by means of a pipe cleaner. Because it was not known whether the liquid clinging to the walls of the sampling tube, centrifuge tube, and capillary pipette had the same composition as the whole distillate sample, it was desirable to know what percentage of the total sample was lost in transfer. The amount of sample remaining in the sampling outlet was determined by weighing a dry pipe cleaner, cleaning the sampling outlet with the cleaner and reweighing it. The centrifuge tube and the capillary pipette were weighed dry and again weighed after the samples were removed. The total weight of sample lost in transfer was thus found to be about 0.1g. The weight of the distillate sample varied from 0.8 to 7g., depending on the size and composition of the still-pot liquid. It is expected then, that the error from this source is small.

A comparison between the Othmer and Hands and Norman stills was accomplished by comparing experimental data from the Hands and Norman still with the smooth curve drawn from data obtained in the Othmer still for the same system. The results, shown in Table V, show good comparison between the two stills.

TABLE V

COMPARISON OF VAPOR-LIQUID EQUILIBRIA AS DETERMINED IN THE HANDS AND NORMAN STILL AND IN THE OTHMER STILL

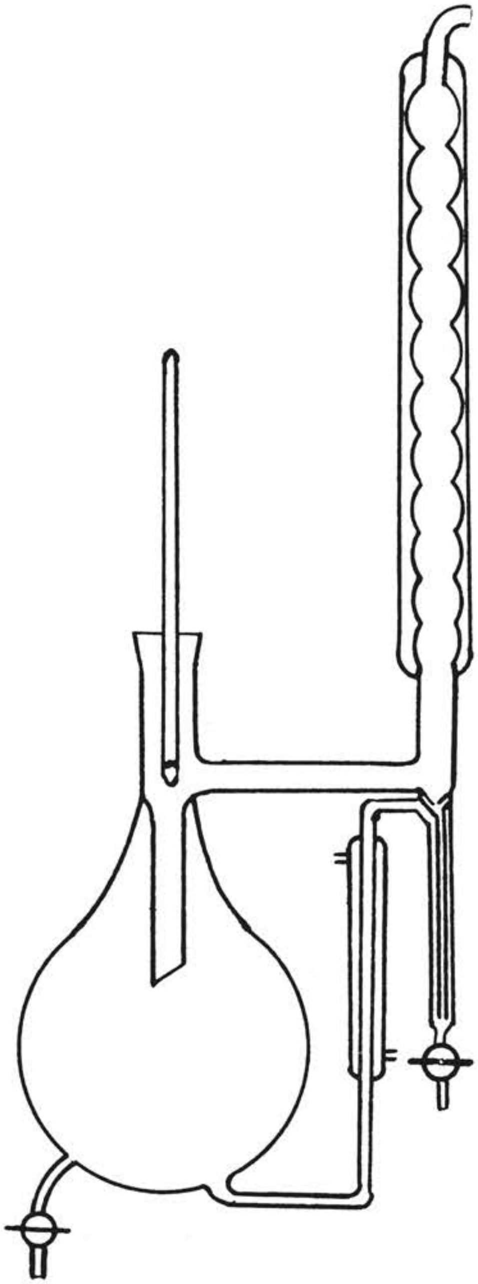
System: Water-Acetic acid

	Wt. % water in	
	Liquid	Vapor
Hands and Norman	34.2	46.3
Othmer	34.2	46.8

System: Acetic acid-Dimethylaniline

	Wt. % Acetic acid	
	Liquid	Vapor
Hands and Norman	49.6	89.6
Othmer	49.6	89.6

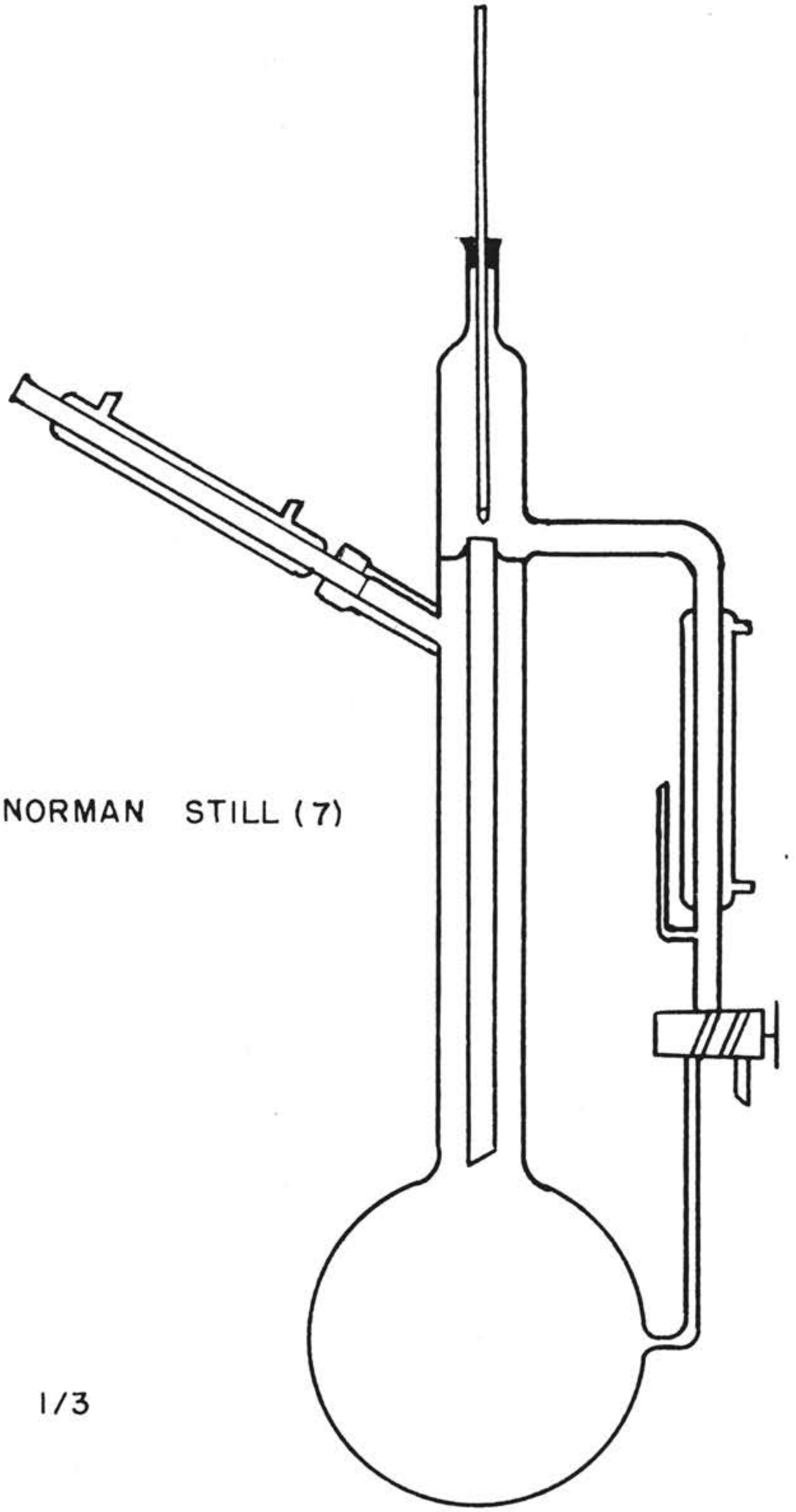
FIG. 3



OTHMER STILL (6)

SCALE = app. 1/3

FIG. 4



HANDS and NORMAN STILL (7)

SCALE = app. 1/3

RESULTS

The first runs were made on the acetic acid-water system with the data being determined in the Othmer still. The data obtained are presented as weight percent water in the vapor versus weight percent water in the liquid in Fig. 5 and in Table VI. With these data are also plotted the data of Othmer and Gilmont[8], those of Cornell and Montonna[9], and those of Garwin and Hutchison[10] for the same system. The curve obtained during this investigation lies very close to the curves of Cornell and Montonna, and Garwin and Hutchison, but is somewhat lower than the curve of Othmer and Gilmont. A comparison of the boiling point data here obtained with those of previous workers appears in Table VII. It may be seen that the boiling points determined during this investigation are about 0.3°C. lower than those recorded by previous workers.

The Othmer still was used for the determination of the vapor-liquid equilibrium for the system acetic acid-dimethylaniline. The data obtained for this system are presented as weight percent acetic acid in the vapor versus weight percent acetic acid in the liquid in Fig. 6 and in Table VIII. The boiling point curve for this system is shown in Fig. 7.

Data for the ternary system were determined in both the Othmer and the Hands and Norman stills. These data are presented as weight percent water in the vapor (on a dimethylaniline-free basis) versus weight percent water in the liquid (on a dimethylaniline free basis) in Fig. 8. The smoothed data for this system appear in Table IX. The curves of Fig. 8 were obtained by drawing the best smooth curve for zero percent dimethylaniline, then taking the approximate ten percent dimethylaniline-in-liquid points, and relocating to exactly ten percent by interpolation or extrapolation (with reference to the zero percent dimethylaniline line) along a line perpendicular to the forty-five degree line. The best ten percent curve was then drawn. The twenty percent points were relocated by interpolation or extrapolation from the smooth ten percent curve and the process continued in this manner.

Boiling point curves for the ternary system are presented in Figs. 9-15 and the smoothed data in Table X.

Representation of dimethylaniline concentration in the vapor as a function of liquid composition is given in Fig. 16 and Table XI. The approximate ten percent dimethylaniline points (in the liquid), were relocated to exactly ten percent by interpolation or extrapolation between the actual percentage points and the abscissa (zero percent line) along a line parallel to the ordinate. The best smooth curve was drawn and the twenty percent points were relocated by interpolation or extrapolation between the approximate twenty percent points and the smoothed ten percent curve. The remaining points were relocated similarly. The complete experimental data for the system water-acetic acid-dimethylaniline appear in Table XII. Hands and Norman still liquid compositions and distillation temperatures are presesented as average values, except for the case of 90% dimethylaniline in the liquid, where initial, final and average values are all given.

future living, educators must supply those subjects that will lend themselves to the all-rounded growth of the individual. Industrial arts is an important part of general education for girls as well as the boys. It has an interesting development from the beginning to the present time.

Industrial Arts and Life. The high school of today can play a large part in the development of the citizens of tomorrow as stated by Mr. John Tate[2], in his thesis of 1949. More than half (sixty percent) of the high school students are not getting the training and preparation needed to make even a moderate success in life. School drop-outs prove that the students are not getting the kind of education that they need and are interested in. Boys are in a development stage of life, either physical or creative, where they can see the immediate results of their efforts. The physical development can be cared for in the athletic program which at the present time is on the increase, and the creative urge or instinct can be developed in the industrial arts program.[2]

Industrial Arts with the many phases or subject areas that it contains is important to the modern secondary schools in America. The practical value of skills that are developed are secondary to the values that are received by the student. The study of industrial arts by the boys and girls is indeed the study of the methods and materials of our modern civilization. Truly the study of industrial arts can be considered

---

[2] John B. Tate, Instructor of School of Industrial Arts Education and Engineering Shopwork. An Analysis of Industrial Arts Education Curriculums in Fifty-One Selected College and Universities in the United States. 1949. Oklahoma Agricultural and Mechanical College, Stillwater, Oklahoma.

TABLE VI

VAPOR-LIQUID EQUILIBRIUM IN THE SYSTEM WATER-ACETIC ACID AT 760 mm.

Experimental Data

Temp. °C.	Wt. % H_2O Vapor	Wt. % H_2O Liquid
100.0	100.0	100.0
100.1	94.6	92.8
100.0	89.7	86.2
100.2	88.1	84.1
100.7	77.9	70.4
100.8	72.6	62.8
101.2	61.6	49.9
102.0	50.7	38.0
102.4	49.9	37.0
103.4	40.3	28.0
105.1	27.6	18.6
105.2	26.2	17.1
107.5	17.9	10.4
108.0	17.1	9.9
115.3	2.5	1.5

Smoothed Data

Temp. °C.	Wt. % H_2O Vapor	Wt. % H_2O Liquid
100.0	100.0	100.0
100.1	92.5	90.0
100.2	85.1	80.0
100.7	77.4	70.0
100.9	70.0	60.0
101.3	62.2	50.0
102.1	52.9	40.0
103.2	42.3	30.0
104.7	30.1	20.0
107.9	16.7	10.0
118.1	0.0	0.0

TABLE VII

SYSTEM: WATER-ACETIC ACID
BOILING POINT VERSUS CONCENTRATION
PRESSURE = 760 mm

	Temp. °C			
X	Othmer & Gilmont	Cornell & Montonna	Garwin & Hutchison	This Investigation
0	118.0	118.1		
10	108.6	108.2	108.2	107.9
20	105.1	105.1	105.1	104.7
30	103.4	103.4	103.4	103.2
40	102.3	102.3	102.3	102.1
50	101.6	101.6	101.7	101.3
60	101.1	101.1	101.2	100.9
70	100.7	100.7	100.8	100.7
80	100.4	100.4	100.5	100.2
90	100.2	100.2	100.2	100.1
100	100.0	100.0	100.0	100.0

X = Weight percent water in the liquid

FIG. 5

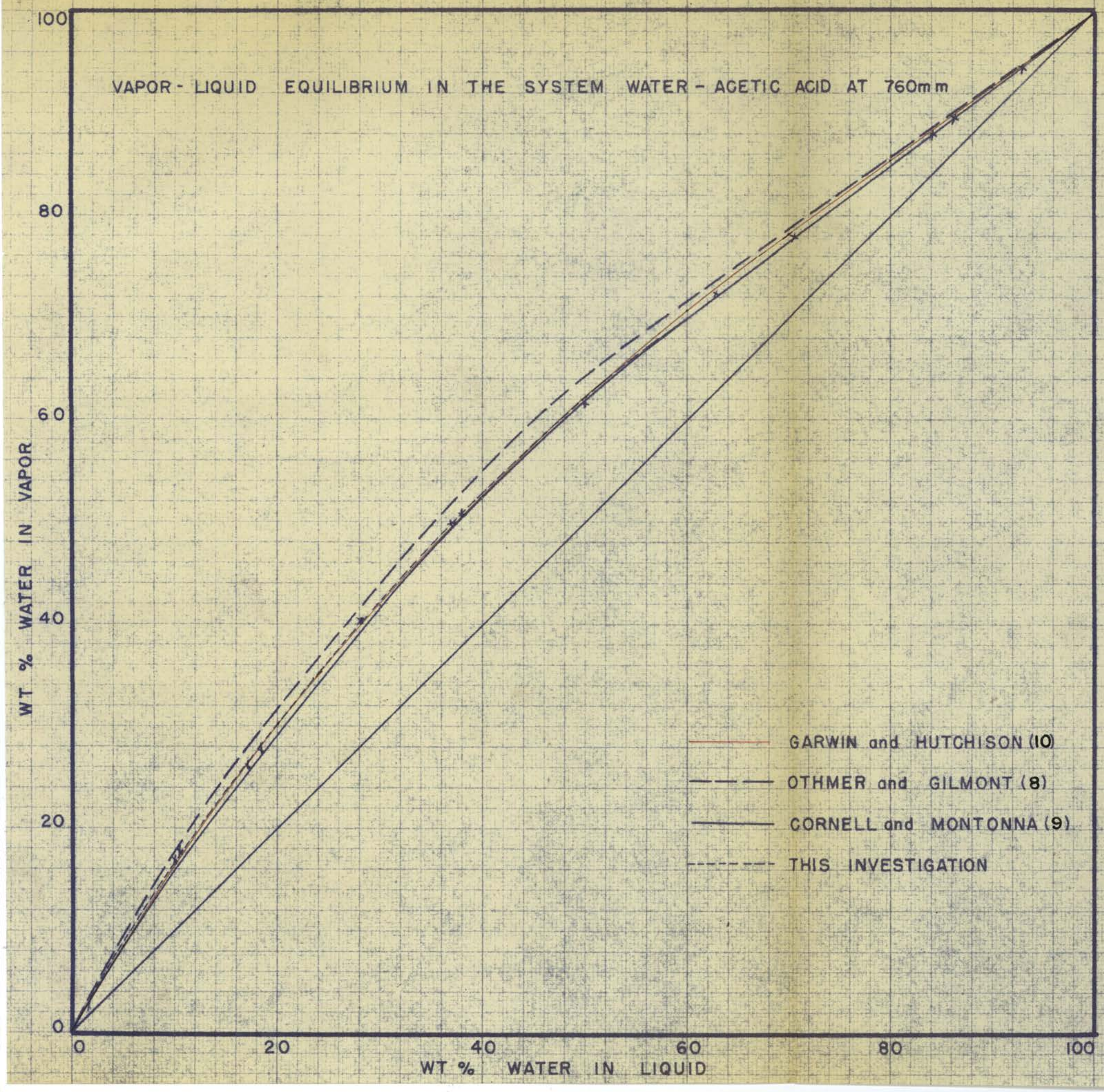

VAPOR - LIQUID EQUILIBRIUM IN THE SYSTEM WATER - ACETIC ACID AT 760mm
WT % WATER IN VAPOR
WT % WATER IN LIQUID
0
20
40
60
80
100
GARWIN and HUTCHISON (10)
OTHMER and GILMONT (8)
CORNELL and MONTONNA (9)
THIS INVESTIGATION

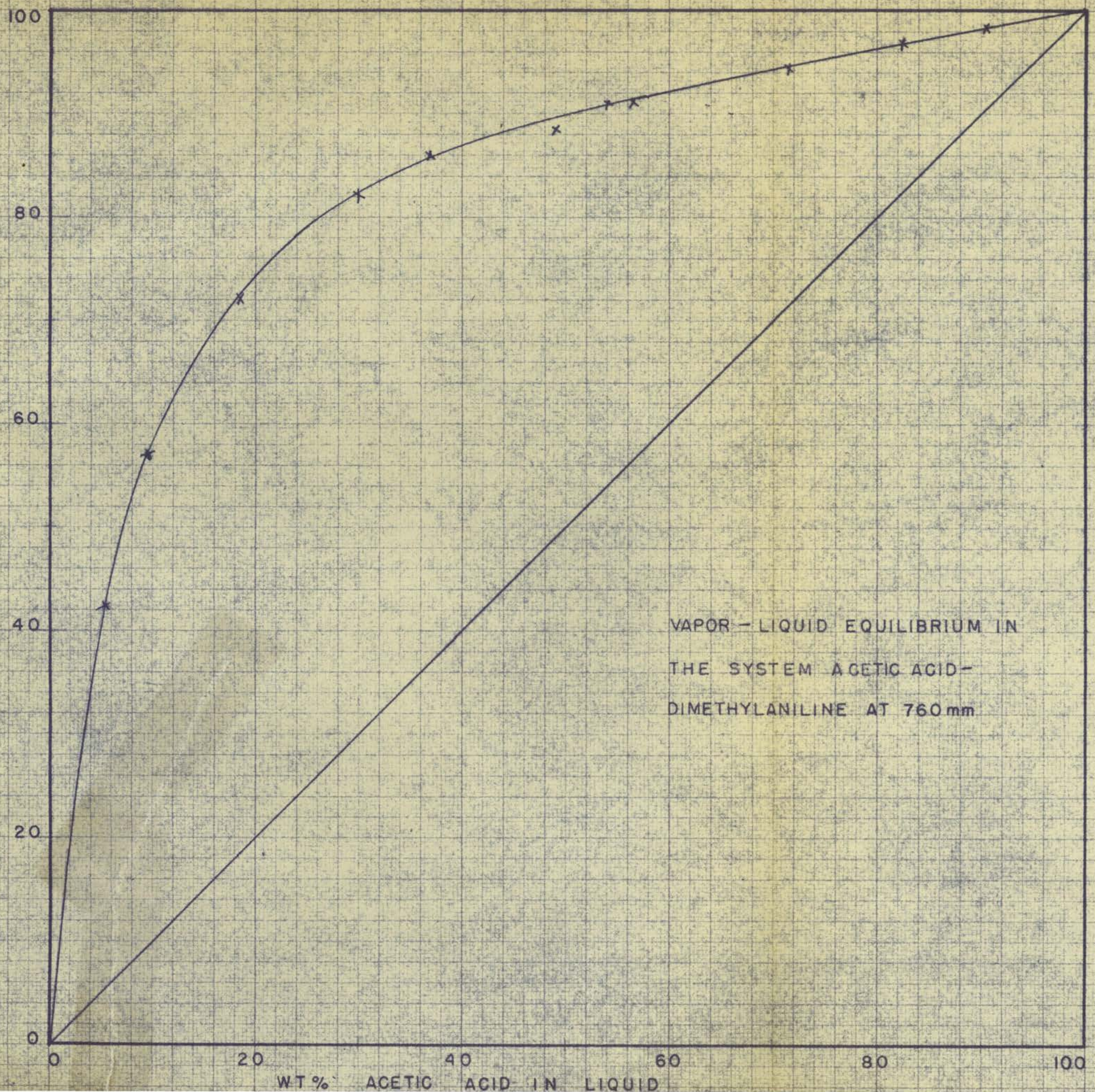
TABLE VIII

SYSTEM: ACETIC ACID-DIMETHYLANILINE
VAPOR-LIQUID EQUILIBRIUM AT 760 mm.

Experimental Data			Smoothed Data		
T	X	Y	T	X	Y
193.0	0.0	0.0	171.0	2.0	19.8
161.0	5.3	42.5	168.3	4.0	34.7
152.6	9.3	57.2	160.5	6.0	45.5
141.6	17.5	72.0	155.0	8.0	53.2
134.0	29.9	82.2	151.3	10.0	58.4
130.8	36.8	86.0	148.4	12.0	62.6
127.9	49.0	88.6	143.6	16.0	69.1
126.2	54.0	91.2	139.7	20.0	74.3
125.4	56.5	91.2	136.7	24.0	78.3
122.2	71.6	94.5	134.6	28.0	81.2
120.0	82.2	97.0	133.0	32.0	83.5
118.0	90.5	98.5	131.5	36.0	85.4
			130.1	40.0	87.0
			127.8	48.0	89.4
			126.0	56.0	91.4
			124.5	64.0	93.0
			123.1	72.0	94.8
			120.3	88.0	97.9
			119.2	94.0	99.0
			118.1	100.0	100.0

X = Weight percent acetic acid in the liquid.
Y = Weight percent acetic acid in the vapor.
T = Temperature, ^{o}C.

FIG. 6



VAPOR – LIQUID EQUILIBRIUM IN THE SYSTEM ACETIC ACID – DIMETHYLANILINE AT 760 mm

FIG. 7

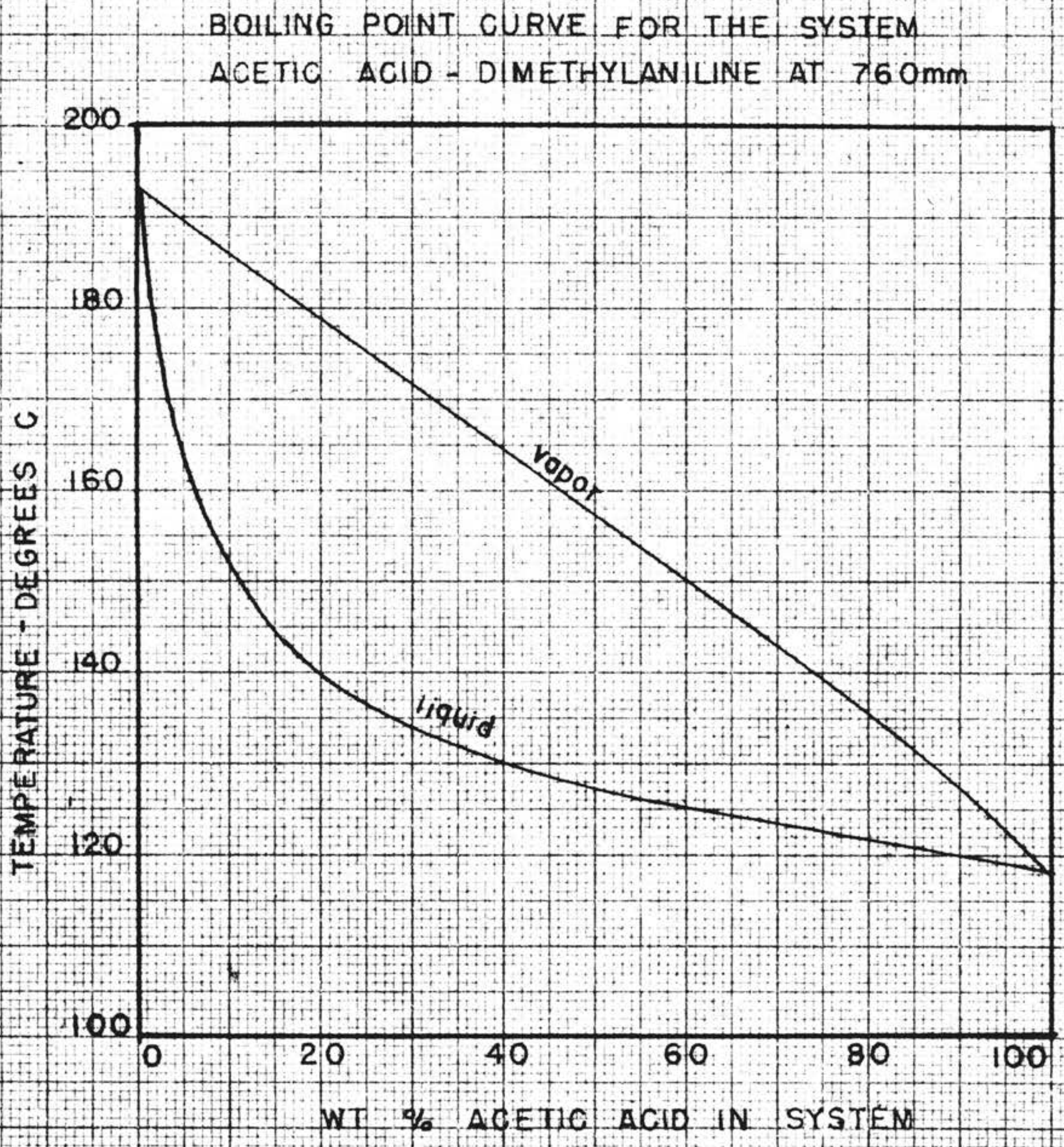

BOILING POINT CURVE FOR THE SYSTEM
ACETIC ACID - DIMETHYLANILINE AT 760mm
200
180
160
140
120
100
TEMPERATURE - DEGREES C
vapor
liquid
0
20
40
60
80
100
WT % ACETIC ACID IN SYSTEM

TABLE IX

VAPOR-LIQUID EQUILIBRIUM
SYSTEM: WATER-ACETIC ACID-DIMETHYLANILINE
PRESSURE = 760 mm
Smoothed Data

X	Y							
	Z = 0	10	20	30	40	50	70	90
4.0	7.4	9.8	11.0	12.2	13.6	16.0	18.6	20.6
8.0	13.6	17.6	19.3	21.8	24.6	29.6	33.8	40.6
12.0	19.6	24.0	27.4	30.4	34.8	40.2	45.4	56.4
16.0	25.0	30.0	34.2	38.6	43.2	48.4	54.3	65.2
20.0	30.1	35.4	40.8	45.8	50.2	54.7	60.1	70.3
24.0	35.1	40.7	47.6	52.2	55.7	59.3	64.1	73.5
28.0	40.0	46.1	53.3	57.5	60.2	62.6	67.0	75.9
32.0	44.4	51.2	58.6	61.6	63.3	65.0	69.2	77.9
36.0	48.8	55.9	63.1	64.9	66.0	67.1	71.2	79.5
40.0	52.9	60.3	66.4	67.5	68.5	69.1	72.9	80.4
44.0	56.7	64.2	69.0	69.9	70.7	70.9	74.5	81.9
48.0	60.4	67.5	71.3	71.1	71.7	71.7	76.1	82.9
52.0	63.9	70.6	73.3	74.1	74.2	74.2	77.6	83.8
56.0	67.0	73.4	75.3	75.9	75.9	75.9	79.1	84.6
60.0	70.0	76.2	77.4	77.7	77.7	77.7	80.8	85.3
64.0	72.9	78.8	79.5	79.7	79.7	79.7	82.6	86.4
68.0	75.9	81.3	81.7	81.8	81.8	81.8	84.3	87.6
72.0	79.1	83.7	83.9	83.9	83.9	83.9	86.2	89.0
76.0	82.0	86.2	86.3	86.3	86.3	86.3	88.0	90.4
80.0	85.1	88.4	88.4	88.4	88.4	88.4	90.0	91.9
84.0	88.1	90.7	90.7	90.7	90.7	90.7	91.9	93.4
88.0	91.0	93.0	93.0	93.0	93.0	93.0	93.8	95.0
92.0	94.2	95.3	95.3	95.3	95.3	95.3	95.9	96.7
96.0	97.1	97.4	97.4	97.4	97.4	97.4	97.9	98.4

X = Weight percent water in the liquid (dimethylaniline-free basis)
Y = Weight percent water in the vapof (dimethylaniline-free basis)
Z = Weight percent dimethylaniline in the liquid

FIG. 8

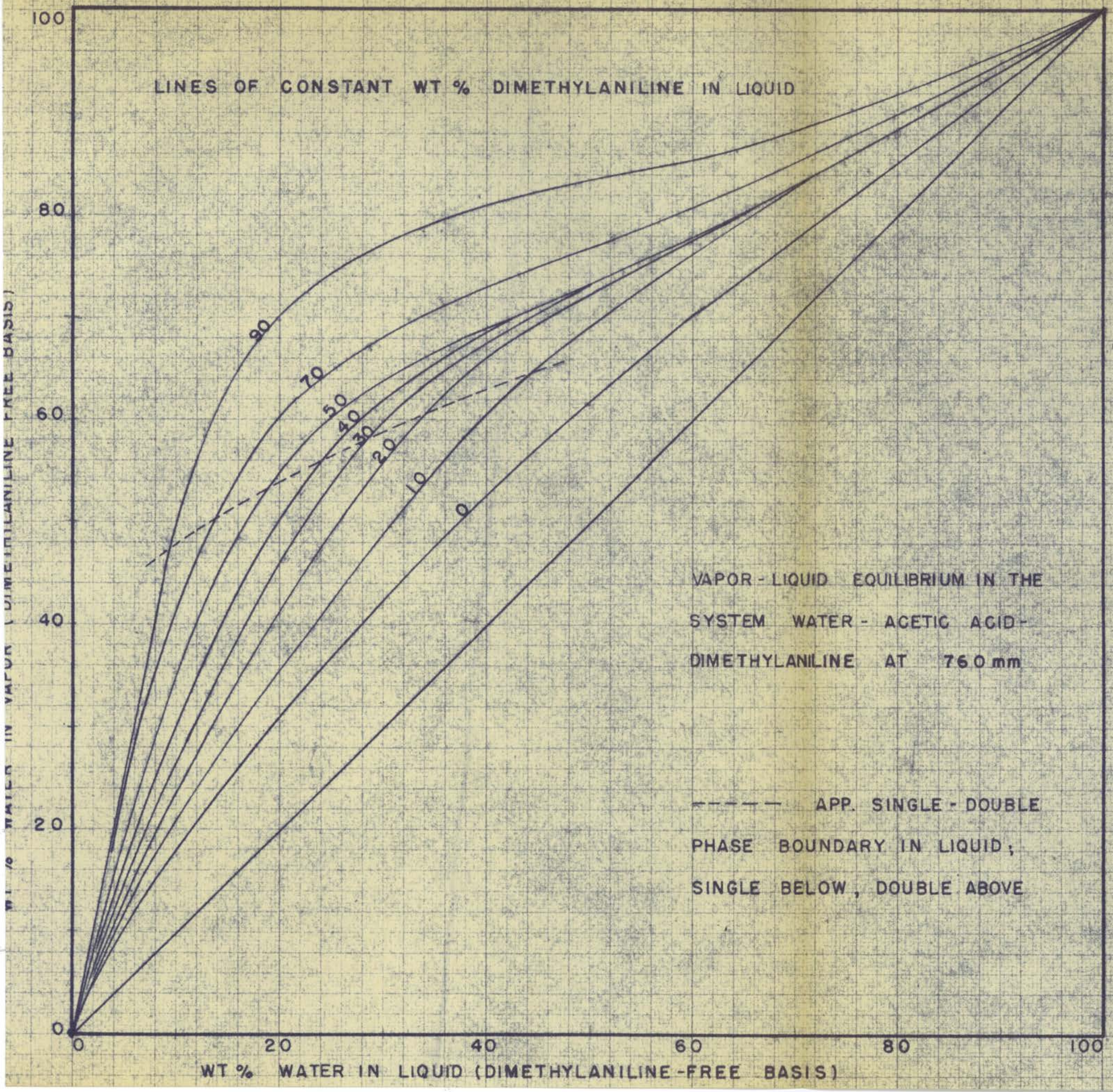

LINES OF CONSTANT WT % DIMETHYLANILINE IN LIQUID
VAPOR - LIQUID EQUILIBRIUM IN THE
SYSTEM WATER - ACETIC ACID -
DIMETHYLANILINE AT 760 mm
APP. SINGLE - DOUBLE
PHASE BOUNDARY IN LIQUID;
SINGLE BELOW, DOUBLE ABOVE
90
70
50
40
30
20
10
0
0
20
40
60
80
100
0
20
40
60
80
100
WT % WATER IN LIQUID (DIMETHYLANILINE-FREE BASIS)
WT % WATER IN VAPOR (DIMETHYLANILINE FREE BASIS)

TABLE X

SMOOTHED BOILING POINT DATA
WATER-ACETIC ACID-DIMETHYLANILINE

	T						
	Weight percent dimethylaniline in liquid						
X	10%	20%	30%	40%	50%	70%	90%
0	120.0	121.8	123.2	125.0	127.0	133.3	152.0
5	113.6	113.7	114.7	115.0	112.2	115.5	123.3
10	109.7	109.4	110.0	109.6	108.7	107.5	111.0
15	107.0	106.5	106.7	105.4	104.7	104.2	104.6
20	105.2	104.7	104.5	103.0	102.8	102.1	102.1
25	104.2	103.6	103.0	101.8	101.8	101.0	100.7
30	103.4	102.7	102.3	101.3	101.5	100.5	100.0
35	102.6	102.0	101.7	101.0	101.2	100.4	99.5
40	102.0	101.3	101.1	100.6	101.0	100.2	99.3
45	101.4	100.7	100.7	100.3	100.7	100.0	99.2
50	100.9	100.3	100.3	100.0	100.4	99.8	99.0
55	100.5	100.0	100.0	99.8	100.2	99.6	98.9
60	100.2	99.6	99.7	99.5	100.0	99.4	98.8
65	99.8	99.3	99.4	99.3	99.7	99.2	98.7
70	99.5	99.0	99.1	99.0	99.4	99.0	98.6
75	99.2	98.8	98.9	98.9	99.3	98.8	98.5
80	98.9	98.6	98.7	98.7	98.9	98.6	98.4
85	98.7	98.4	98.5	98.5	98.7	98.5	98.3
90	98.5	98.3	98.3	98.3	98.5	98.3	98.2
95	98.3	98.1	98.1	98.1	98.2	98.1	98.1
100	98.0	98.0	98.0	98.0	98.0	98.0	98.0

X = Weight percent water in the liquid (dimethylaniline-free basis).

T = Temperature, °C.

BOILING POINT CURVES FOR THE SYSTEM WATER-ACETIC ACID- DIMETHYLANILINE AT 760 mm

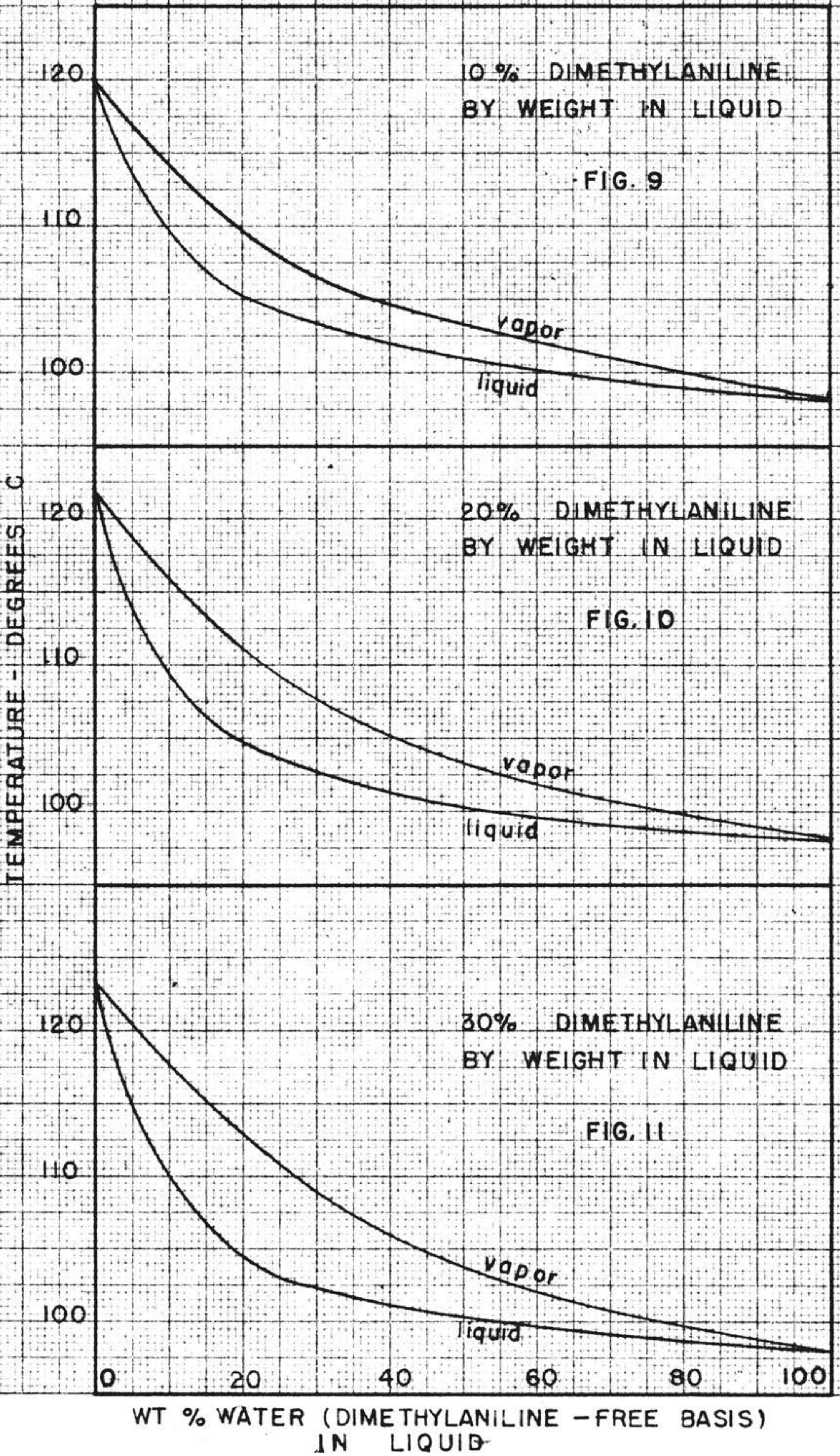
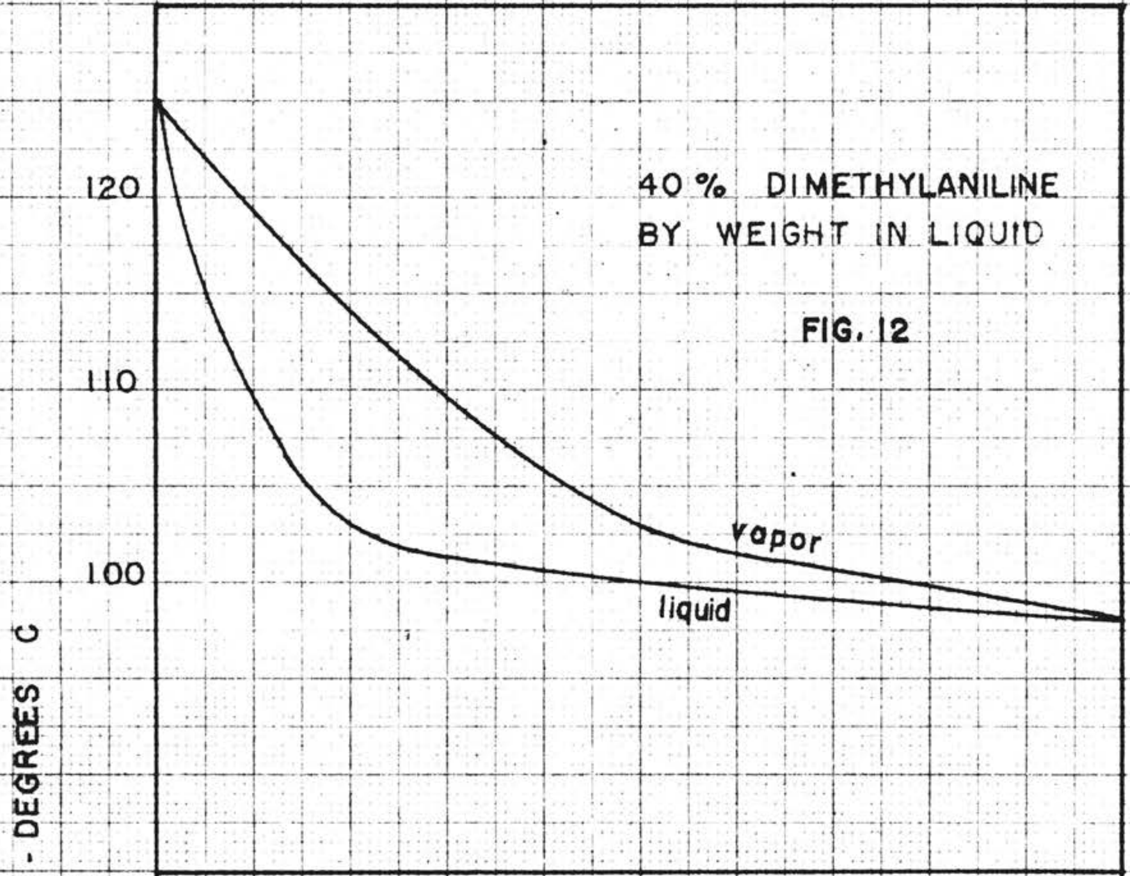


FIG. 9

FIG. 10

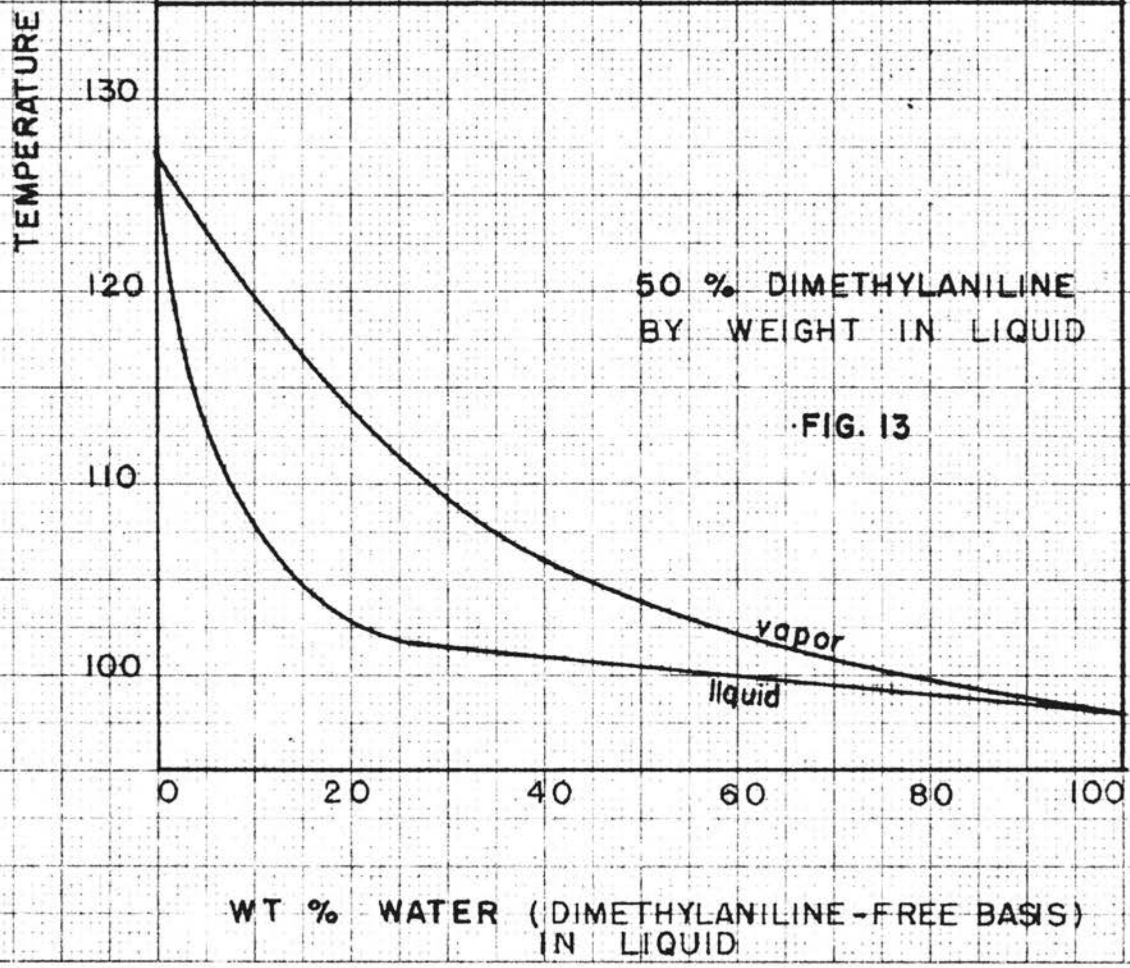
FIG. 11

BOILING POINT CURVES FOR THE SYSTEM WATER-ACETIC ACID - DIMETHYLANILINE AT 760 mm



40 % DIMETHYLANILINE BY WEIGHT IN LIQUID

FIG. 12



50 % DIMETHYLANILINE BY WEIGHT IN LIQUID

FIG. 13

BOILING POINT CURVE FOR THE SYSTEM WATER-ACETIC ACID- DIMETHYLANILINE AT 760mm

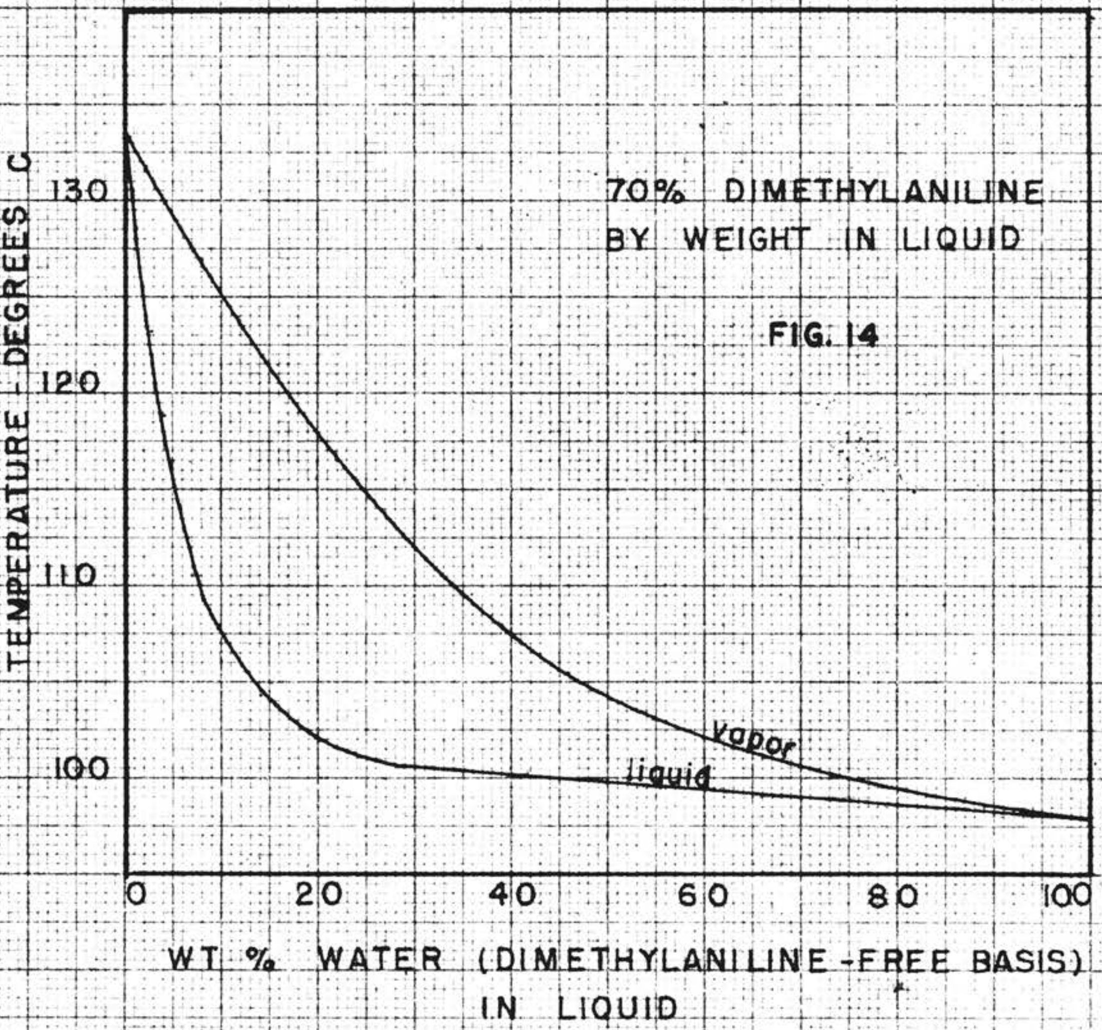


FIG. 14

BOILING POINT CURVE FOR THE SYSTEM WATER-ACETIC ACID- DIMETHYLANILINE AT 760 mm

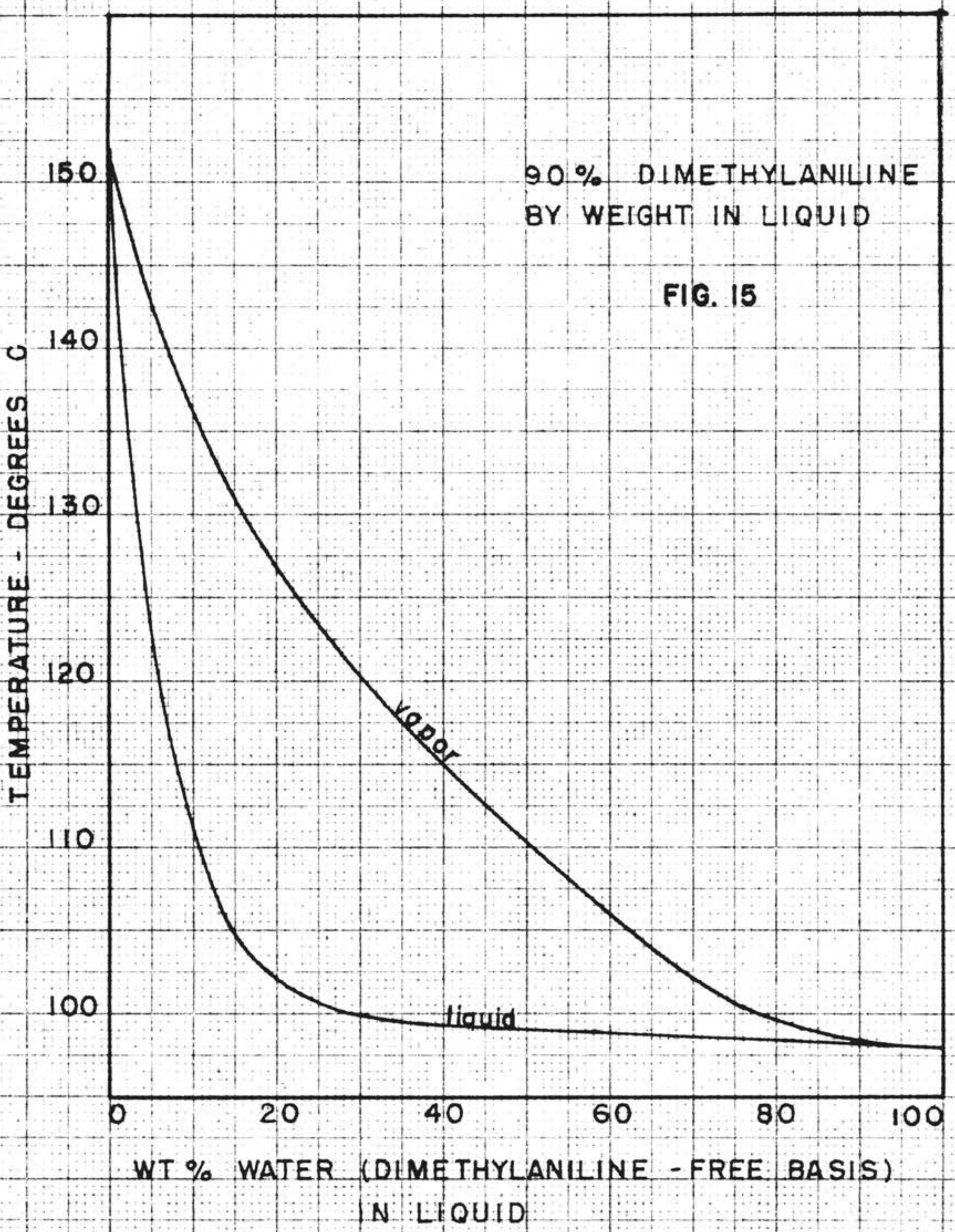


FIG. 15

TABLE XI

DIMETHYLANILINE VAPOR CONCENTRATIONS IN THE SYSTEM WATER-ACETIC ACID-DIMETHYLANILINE (SMOOTHED DATA)

		B					
X	Z =	10%	20%	30%	50%	70%	90%
0		1.3	3.5	5.5	10.3	22.0	42.5
5		1.4	4.2	6.8	9.6	15.0	27.5
10		1.7	5.4	8.3	10.1	14.9	22.8
15		2.2	6.2	9.8	12.7	16.0	20.7
20		2.8	8.4	11.5	14.8	17.1	20.0
25		3.5	10.3	13.3	16.6	18.0	19.9
30		4.6	12.3	15.3	17.9	18.8	19.9
35		6.1	14.7	17.2	18.7	19.5	19.8
40		8.0	17.2	18.8	19.2	19.9	19.9
45		10.4	19.1	19.5	19.5	19.9	19.9
50		13.5	19.5	19.5	19.5	20.0	20.1
55		17.2	19.6	19.6	19.6	20.0	20.2
60		19.1	19.6	19.6	19.6	20.0	20.5
65		19.7	19.7	19.7	19.7	20.0	20.8
70		19.7	19.7	19.7	19.7	20.1	21.1
75		19.8	19.8	19.8	19.8	20.2	21.5
80		19.8	19.8	19.8	19.8	20.3	21.9
85		19.9	19.9	19.9	19.9	20.4	22.3
90		20.0	20.0	20.0	20.0	20.6	22.8

X = Weight percent water in liquid (dimethylaniline free basis).

Z = Weight percent dimethylaniline in the liquid.

B = Weight percent dimethylaniline in the vapor.

FIG. 16

DIMETHYLANILINE VAPOR CONCENTRATIONS
IN THE SYSTEM WATER - ACETIC ACID -
DIMETHYLANILINE AT 760 mm

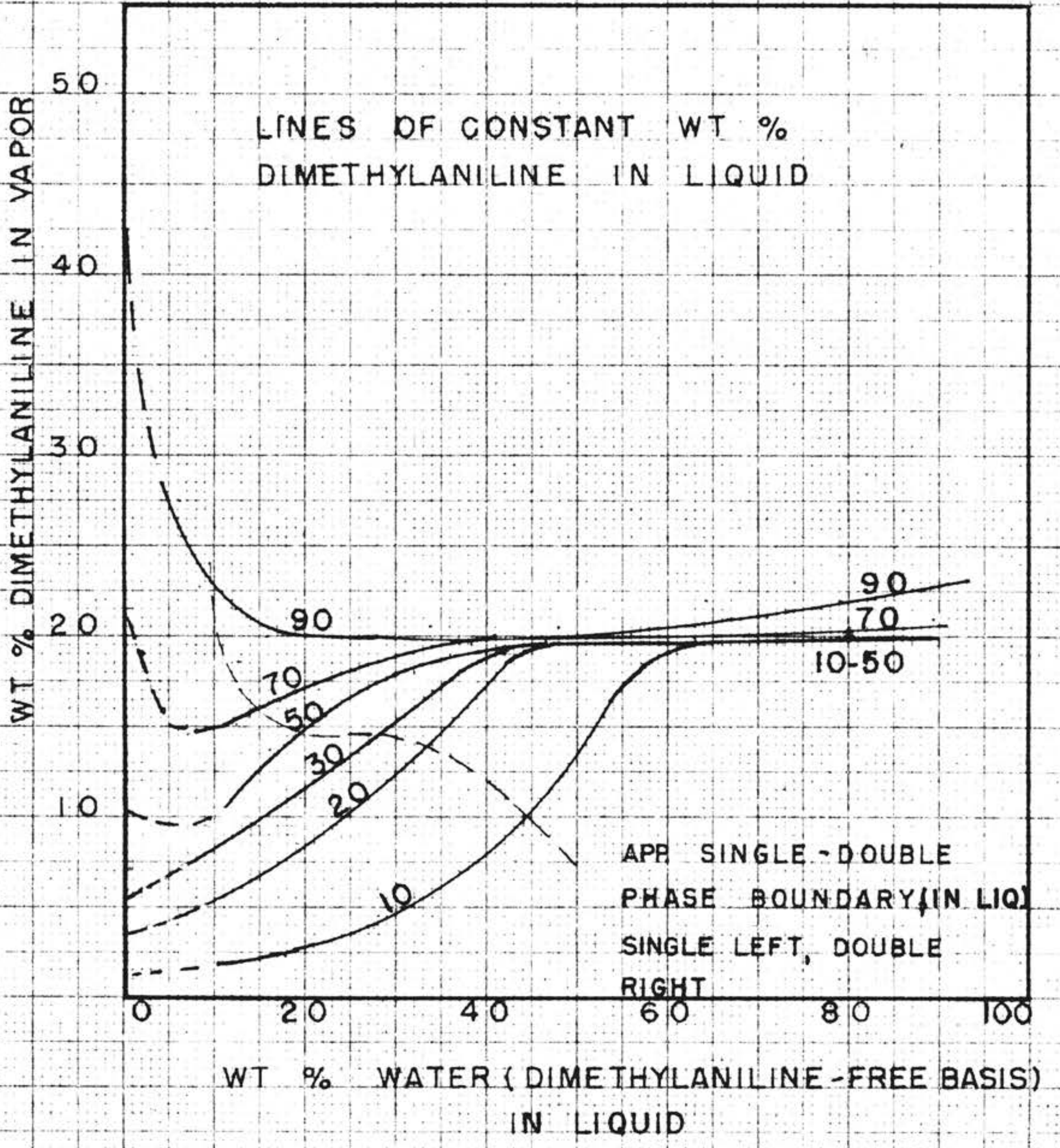


TABLE XII

VAPOR-LIQUID EQUILIBRIUM IN THE SYSTEM: WATER-ACETIC ACID-DIMETHYLANILINE AT 760 mm. EXPERIMENTAL DATA

Temp. °C.	HAc	DMA	H_2O	HAc	DMA	H_2O	Nx	Ny	S	Weight % H_2O DMA free basis	
	(Wt. % in Liq)			(Wt. % in Vap.)						Liq.	Vapor
Dimethylaniline in liquid approximately ten weight percent											
98.5	5.2	9.5	85.3	2.8	19.8	77.4	2	2	H	94.2	96.5
98.5	9.9	9.8	81.3	5.3	19.5	75.2	2	2	H	89.0	93.4
99.0	14.2	9.2	76.6	7.4	19.4	73.2	2	2	H	84.4	90.8
99.1	18.1	9.4	72.5	9.6	19.5	70.9	2	2	H	80.0	88.1
99.4	21.8	8.9	69.3	11.0	20.2	68.8	2	2	H	76.1	86.2
99.5	25.1	9.1	65.8	13.2	19.7	67.1	2	2	H	72.4	83.6
99.7	30.4	10.3	59.3	16.2	19.1	64.7	2	2	H	66.1	80.0
100.1	35.1	10.8	54.1	18.4	19.0	62.6	2	2	H	60.6	77.3
100.3	39.6	10.1	50.3	20.9	17.5	61.6	2	2	H	55.9	74.6
100.6	42.8	9.8	47.4	24.4	15.6	60.0	2	2	H	52.6	71.1
101.0	46.3	9.7	44.0	27.8	12.3	59.9	1	2	H	48.5	68.4
101.6	51.9	8.5	39.6	34.6	7.8	57.6	1	1	O	43.3	62.5
101.9	54.6	9.6	35.8	37.5	6.0	56.5	1	1	O	39.6	60.1
103.0	61.5	9.6	28.9	46.2	5.6	48.2	1	1	O	32.0	51.1
103.0	61.5	9.5	29.0	46.9	5.6	47.5	1	1	O	32.0	50.4
104.4	68.3	10.0	21.7	58.0	4.0	38.0	1	1	O	23.1	39.6
105.0	69.7	11.1	19.2	60.9	3.9	36.2	1	1	O	20.5	37.7
107.0	76.2	10.9	13.0	71.1	2.8	26.1	1	1	O	14.7	26.9
116.0	81.2	13.9	4.9	83.4	3.1	13.6	1	1	O	5.7	14.0
Dimethylaniline in liquid approximately twenty weight percent											
98.0	5.2	20.1	74.7	3.2	20.8	76.0	2	2	H	93.5	96.0
98.0	10.9	19.8	69.3	6.5	20.0	73.5	2	2	H	86.4	91.9
98.8	15.9	19.5	64.6	9.7	20.0	70.3	2	2	H	80.3	87.9
99.0	20.4	19.2	60.4	12.1	20.5	67.4	2	2	H	74.7	84.8
99.7	24.6	18.9	56.5	14.1	20.1	65.8	2	2	H	69.7	82.3
99.8	28.0	18.6	53.4	15.6	20.0	64.4	2	2	H	65.6	80.5
100.0	33.7	19.7	46.6	19.6	18.7	61.7	2	2	H	58.0	75.9
100.4	38.8	19.3	41.9	22.0	18.9	59.3	2	2	H	51.7	73.1
100.9	42.9	18.9	38.2	24.2	18.7	57.1	2	2	H	47.1	70.4

Nx = Number of phases present in the liquid
Ny = Number of phases present in the condensed vapor
S = Type of still used (Othmer or Hands & Norman)
O = Othmer
H = Hands & Norman

TABLE XII (cont.)

Temp °C.	HAc	DMA	H_2O	HAc	DMA	H_2O	Nx	Ny	S	Weight % H_2O DMA free basis	
	(Wt. % in Liq)			(Wt. % in Vap.)						Liq.	Vapor
Dimethylaniline in liquid approximately twenty weight percent (cont)											
101.1	46.5	18.8	34.7	26.0	18.0	56.0	2	2	H	42.7	68.3
101.5	49.5	18.6	31.9	28.2	16.1	55.7	2	2	H	39.1	66.4
101.9	52.2	18.4	29.4	32.8	14.1	53.1	1	2	H	36.1	61.8
101.4	54.5	20.4	25.1	36.2	12.8	51.0	1	1	H	31.7	58.5
103.3	60.8	20.3	18.9	47.6	8.8	43.6	1	1	H	23.7	47.8
104.2	60.5	21.3	18.2	48.1	10.0	41.9	1	1	O	23.0	46.6
104.7	64.5	20.2	15.3	55.6	8.1	36.3	1	1	H	19.1	39.6
107.0	68.9	20.2	10.9	66.2	5.4	28.4	1	1	H	13.7	30.0
107.6	67.7	21.2	10.1	65.5	7.2	27.3	1	1	O	14.0	29.5
109.5	73.8	20.3	5.9	78.7	3.9	17.4	1	1	H	7.5	18.1
111.8	74.2	21.1	4.7	80.3	4.8	14.9	1	1	O	6.0	15.8
Dimethylaniline in liquid approximately 30 weight percent											
98.0	7.5	34.7	57.3	5.7	19.7	74.3	2	2	H	88.5	92.9
98.0	13.7	34.0	52.3	10.1	20.0	69.9	2	2	H	79.1	87.4
99.0	18.7	34.2	47.1	13.0	19.2	67.8	2	2	H	71.7	83.9
99.2	23.1	33.9	43.0	15.6	18.5	65.9	2	2	H	65.2	80.9
99.9	26.7	34.3	39.0	18.2	19.5	62.3	2	2	H	59.5	77.4
100.0	30.0	33.9	36.1	20.0	19.0	61.0	2	2	H	54.7	75.3
100.5	35.1	33.6	31.3	22.8	18.7	58.5	2	2	H	47.3	72.0
100.8	39.1	33.5	27.4	25.4	18.8	55.8	2	2	H	41.3	68.7
101.2	42.4	33.4	24.2	28.3	17.8	54.0	2	2	H	36.5	65.5
101.9	45.1	33.3	21.6	30.5	17.4	52.1	2	2	H	33.5	63.1
102.2	47.1	33.3	19.6	33.5	16.0	50.5	2	2	H	29.4	60.1
103.0	49.0	33.3	17.7	36.2	15.8	48.0	1	2	H	26.6	57.0
104.6	53.1	34.0	12.9	45.9	13.2	40.9	1	1	O	19.5	47.1
108.0	58.8	32.6	9.6	59.6	10.4	30.0	1	1	O	12.6	33.5
108.4	58.6	33.5	7.9	61.5	10.0	28.5	1	1	O	11.8	31.7
112.4	63.5	31.8	4.7	74.1	8.3	17.6	1	1	O	7.0	19.2
Dimethylaniline in liquid approximately 40 Wt percent											
98.6	6.5	40.4	53.1	5.5	21.0	73.5	2	2	H	89.0	93.0
99.0	12.0	40.3	47.7	9.2	21.0	69.8	2	2	H	80.0	88.4
99.4	20.8	41.3	37.9	16.1	19.8	64.1	2	2	H	64.5	79.9
99.6	20.3	40.0	39.7	14.7	20.4	64.9	2	2	H	66.2	81.5
99.6	20.3	40.2	39.5	15.1	20.5	64.4	2	2	H	66.1	81.0
99.6	23.6	41.4	35.0	17.4	19.6	63.0	2	2	H	59.7	78.3
99.8	23.5	40.0	36.5	17.2	19.7	63.1	2	2	H	60.9	78.6
100.0	27.3	41.6	31.1	20.0	19.5	60.5	2	2	H	46.5	75.2
100.3	31.9	42.1	26.0	23.5	18.5	58.0	2	2	H	44.8	71.2
100.6	33.9	41.1	25.0	25.1	18.3	56.7	2	2	H	42.4	69.3
101.0	37.4	41.1	21.5	27.1	18.2	54.5	2	2	H	36.4	66.9
101.7	41.8	41.0	17.2	32.3	17.2	50.5	2	2	H	29.2	61.0
102.0	45.4	42.0	12.6	40.0	15.0	45.0	1	1	H	21.8	53.0
107.2	51.8	40.9	7.3	57.2	9.5	33.5	1	1	H	12.5	37.0

TABLE XII (cont)

Temp. °C.	HAc	DMA	H_2O	HAc	DMA	H_2O	Nx	Ny	S	Weight % H_2O DMA free basis	
	Wt. % in Liquid			Wt. % in Vapor						Liq.	Vapor
Dimethylaniline in liquid approximately 50 weight percent											
98.3	4.1	50.1	45.8	4.3	19.2	76.5	2	2	H	91.8	94.6
98.7	8.7	50.0	41.3	8.8	20.2	71.0	2	2	H	82.6	89.0
99.4	12.5	50.0	37.5	12.1	20.0	67.9	2	2	H	74.9	84.9
99.8	15.9	49.9	34.2	14.8	19.5	65.8	2	2	H	68.3	81.8
99.9	18.5	50.0	31.5	17.1	19.0	63.9	2	2	H	62.9	78.9
99.9	18.8	50.9	30.3	17.0	19.3	78.8	2	2	H	61.8	78.8
100.0	20.0	50.8	29.2	18.3	20.0	61.7	2	2	H	59.3	77.1
100.0	21.0	49.9	29.1	19.2	19.5	61.3	2	2	H	58.1	76.2
100.0	21.4	50.7	27.9	19.4	19.3	61.3	2	2	H	56.5	76.0
100.1	23.2	50.4	26.4	20.7	19.5	59.8	2	2	H	53.1	74.3
100.4	25.0	50.3	24.7	22.5	19.2	58.3	2	2	H	49.7	72.1
100.6	27.3	50.2	22.5	24.3	18.8	56.9	2	2	H	45.2	70.1
100.9	30.0	50.1	19.9	25.3	19.0	55.7	2	2	H	39.8	68.8
101.5	33.9	50.2	15.9	29.5	18.0	52.5	2	2	H	31.9	64.0
101.8	36.3	50.0	13.7	31.9	16.6	51.5	2	2	H	27.4	61.8
102.4	39.1	49.8	11.1	35.3	15.6	49.1	1	2	H	22.1	58.2
104.4	42.2	49.6	8.2	44.6	13.4	42.0	1	1	H	16.2	48.4
107.2	45.9	49.4	4.7	58.4	9.1	32.5	1	1	H	9.2	35.8
Dimethylaniline in liquid approximately 70 weight percent											
98.3	2.9	69.4	27.7	4.1	21.2	74.7	2	2	H	90.2	94.9
98.7	5.5	69.3	25.2	7.7	19.5	72.8	2	2	H	81.8	90.5
99.1	7.8	69.2	23.0	10.1	19.7	70.2	2	2	H	74.6	87.5
99.5	9.8	69.1	21.1	12.5	19.0	68.5	2	2	H	68.4	84.5
99.6	11.4	69.1	19.5	14.1	20.1	65.6	2	2	H	63.1	82.0
99.7	13.0	69.0	18.0	16.0	20.1	63.9	2	2	H	58.2	80.0
99.7	15.3	65.1	19.6	16.6	19.5	61.0	2	2	H	56.3	79.4
99.9	16.2	65.8	18.0	18.0	20.1	61.9	2	2	H	52.5	77.4
99.9	17.4	66.5	16.1	19.5	19.5	61.0	2	2	H	48.2	75.8
100.0	18.7	67.1	14.2	21.7	18.7	59.6	2	2	H	43.3	73.5
100.5	20.6	67.2	12.2	23.1	19.7	57.2	2	2	H	37.8	71.4
100.5	21.3	68.4	10.3	24.1	17.9	69.5	2	2	H	32.5	69.5
101.0	22.5	68.4	9.1	27.1	18.3	54.6	2	2	H	28.7	66.9
101.4	23.0	69.1	7.9	28.5	18.2	53.3	2	2	H	25.4	65.1
101.9	24.2	69.2	6.6	32.0	17.0	51.0	2	2	H	21.5	61.5
102.8	25.1	69.7	5.2	35.9	16.4	47.7	1	2	H	17.3	56.8
105.0	26.4	69.9	3.7	44.6	15.2	40.2	1	1	H	12.5	47.1
111.1	27.5	70.4	2.1	58.0	14.6	27.4	1	1	H	7.0	32.1

TABLE XII (cont.)

	Temp. °C	HAc	DMA	H_2O	HAc	DMA	H_2O	Nx	Ny	S	Weight % H_2O DMA free basis	
		(Wt. % in Liq.)			(Wt. % in Vap.)						Liq.	Vapor
	Dimethylaniline in liquid approximately ninety weight percent											
	98.0	0.68	89.9	9.4	2.0	23.2	74.8	2	2	H	93.3	97.5
	98.2	0.68	90.2	9.1							93.2	
*	98.1										* 93.3	97.5
	98.0	1.32	89.5	9.2	3.8	22.5	73.7	2	2	H	87.4	95.1
	98.1	1.30	90.0	8.7							87.0	
*	98.1										* 87.2	95.1
	98.1	1.93	89.5	8.6	5.9	21.5	72.6	2	2	H	82.6	92.5
	98.2	1.95	89.8	8.2							80.9	
*	98.2										* 81.8	92.5
	98.5	2.60	89.2	8.2	7.7	19.5	72.8	2	2	H	76.0	90.5
	98.5	2.56	89.7	7.7							73.1	
*	98.5										* 74.6	90.5
	98.8	3.33	90.0	6.7	9.1	21.0	69.9	2	2	H	69.8	88.5
	98.8	3.31	89.3	7.4							69.1	
*	98.8										* 69.5	88.5
	99.2	4.04	88.6	7.4	10.8	21.9	67.3	2	2	H	64.6	86.3
	99.2	4.00	88.9	7.7							63.9	
*	99.2										* 64.3	86.3
	99.2	4.8	88.3	6.90	12.0	20.0	68.0	2	2	H	58.7	85.0
	99.3	4.8	88.6	6.64							57.9	
*	99.3										* 58.3	85.0
	99.2	5.8	88.6	5.62	13.5	20.5	66.0	2	2	H	49.5	83.0
	99.3	5.9	88.7	5.38							47.8	
*	99.3										* 48.6	83.0
	99.3	5.9	89.1	5.00	14.2	20.2	65.6	2	2	H	45.7	82.3
	99.3	6.0	89.3	4.66							43.5	
*	99.3										* 44.6	82.3
	99.4	6.3	89.4	4.27	15.1	20.8	64.1	2	2	H	40.1	81.0
	99.5	6.4	89.7	3.93							38.3	
*	99.5										* 39.2	81.0
	99.8	6.8	89.5	3.66	16.0	20.5	62.5	2	2	H	34.8	78.5
	99.8	6.8	89.5	3.34							32.8	
*	99.8										* 33.8	78.5

Note:

Liquid compositions and distillation temperatures are recorded before and after removal of distillate samples.

TABLE XII (cont.)

	Temp. °C.	HAc	DMA	H_2O	HAc	DMA	H_2O	Nx	Ny	S	Weight % H_2O DMA free basis	
		(Wt. % in Liq.)			(Wt. % in Vap.)						Liq.	Vapor
	100.5	7.5	89.6	2.94	20.7	20.0	59.3	2	2	H	28.1	74.1
	101.0	7.4	90.0	2.59							25.9	
*	100.8										* 27.0	74.1
	101.8	7.9	89.9	2.16	23.9	21.4	54.7	2	2	H	21.4	69.6
	102.4	7.8	90.3	1.90							19.6	
*	102.1										* 20.5	69.6
	103.6	8.2	90.1	1.67	27.9	20.1	52.0	2	2	H	16.8	65.1
	105.1	8.1	90.5	1.39							14.5	
*	104.4										* 15.7	65.1
	102.0	9.2	89.0	1.79	30.3	20.1	49.6	2	2	H	16.3	62.0
	103.1	9.0	89.4	1.64							14.8	
*	102.6										* 15.6	62.0
	105.5	8.6	90.0	1.35	32.2	21.6	46.3	2	2	H	13.5	59.0
	107.3	8.5	90.3	1.15							11.8	
*	106.4										* 12.7	59.0
	104.3	9.3	89.3	1.41	34.0	18.7	47.3	2	2	H	13.2	58.3
	105.9	9.2	89.5	1.29							12.3	
*	105.1										* 12.8	58.3
	110.8	9.1	90.0	0.88	40.8	22.8	36.4	1	2	H	8.8	47.1
	112.6	8.9	90.3	0.77							7.9	
*	111.7										* 8.4	47.1
	111.0	9.5	89.5	1.02	42.8	21.6	35.6	2	2	H	9.8	45.5
	114.2	9.4	89.7	0.88							8.9	
*	112.6										* 9.4	45.5
	118.2	9.7	89.6	0.73	50.5	25.5	24.0	1	1	H	7.0	32.2
	119.8	9.5	89.8	0.66							6.5	
*	119.0										6.7	32.2
	120.1	9.8	89.5	0.68	51.0	27.5	21.5	1	1	H	6.5	29.6
	123.2	9.6	89.8	0.60							5.8	
*	122.2										* 6.2	29.6
	126.2	9.8	89.8	0.41	58.3	27.5	14.2	1	1	H	4.0	19.6
	127.8	9.7	89.9	0.38							3.8	
*	127.0										* 3.9	19.6

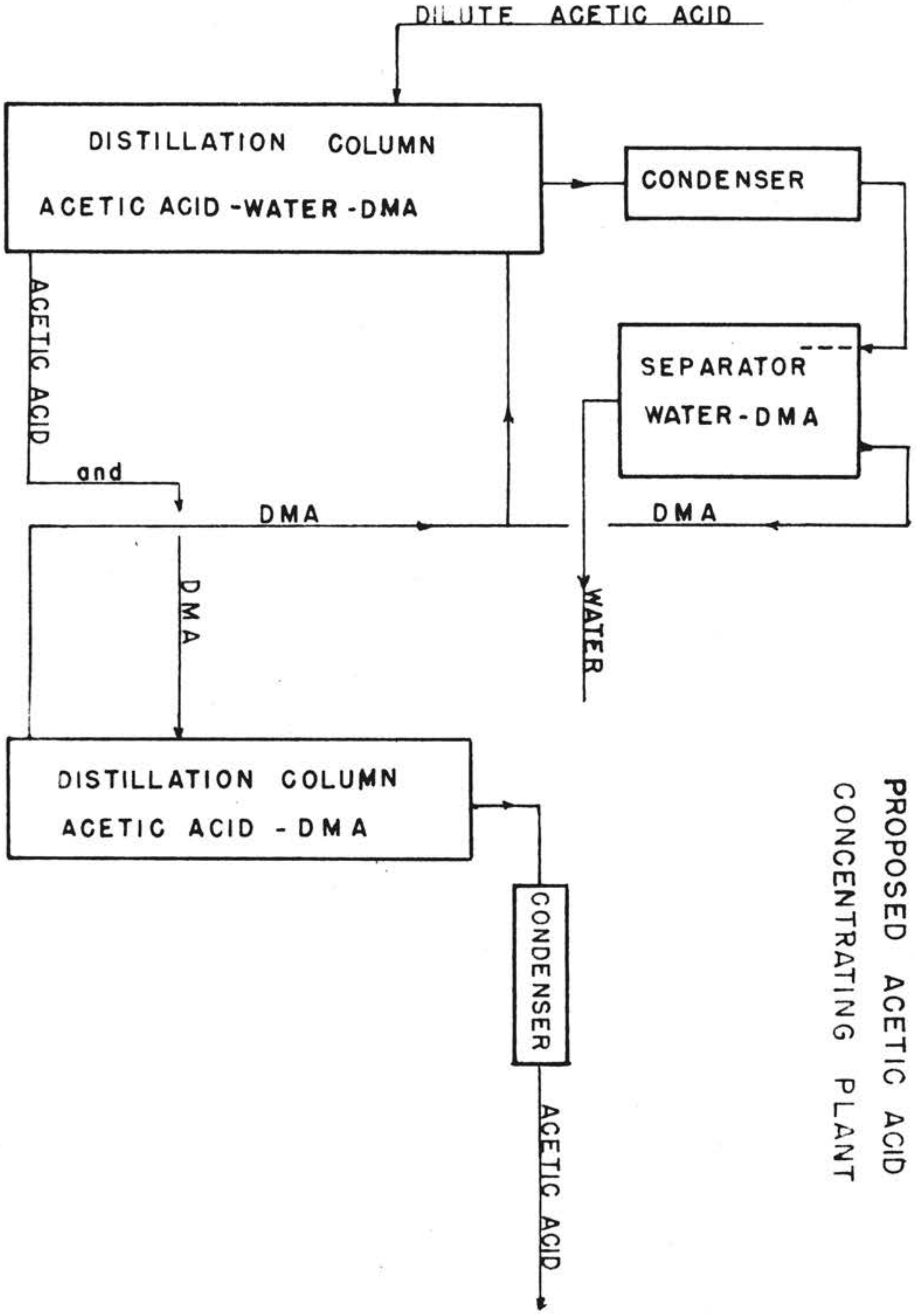
* Indicates the average values of distillation temperatures and liquid compositions.

DISCUSSION

The data show that the addition of dimethylaniline increases markedly the relative volatility of water to acetic acid, particularly in the acetic acid-rich region.

A proposed scheme for separating acetic acid and water by extractive distillation with dimethylaniline is shown in Fig. 17. The dilute acetic acid is distilled in the first column in the presence of dimethylaniline. The distillate from this still consists of water and dimethylaniline which separate on condensing. The water is discarded and the dimethylaniline is recycled to the column. The bottoms product, consisting of acetic acid and dimethylaniline, is charged to a second still where the acetic acid is removed from the top. The dimethylaniline bottoms stream is recycled to the first still. Whether a commercial process utilizing this principle could compete economically with existing processes would require the aquisition of data on the extractive distillation carried out continuously, followed by a detailed economic study.

Factors which would come under consideration, in addition to the increased relative volatility and its consequent effect on the size of equipment, are steam requirements and materials of construction. A suitable material of construction for the dimethylaniline recovery column, where no water would be present, might be aluminum. It is possible that the first column could be constructed of mild steel, since an excess of dimethylaniline could be present. If this is unsatisfactory, stainless steel or any other alloy commonly employed for acetic acid service could be used.



PROPOSED ACETIC ACID CONCENTRATING PLANT

FIG. 17

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APPENDIX

A procedure for the determination of aniline by bromination, as developed in preliminary work, is as follows:[14,15,16]

The sample containing aniline is diluted to 200 ml. in a glass stoppered bottle. The $KBrO_3$-KBr solution (0.1 M $KBrO_3$-0.5M KBr) is added in an amount to give a slight excess of Br_2. One half ml. of concentrated HCl is added for every ml. of $KBrO_3$-KBr solution and the flask is stoppered and let stand for five to ten mintues during which time the following reaction takes place:

After this time the flask is opened and the free bromine is treated with excess KI to give free iodine. The iodine is titrated with $Na_2S_2O_3$ (0.1N-containing 3.8 grams per liter of borax as a preservative)[13] and fresh starch solution indicator is added near the end of the titration.

If, after back titrating, it is found that more than 1 ml. of excess $KBrO_3$-KBr was used per 100 ml. of diluted sample, the amount of $KBrO_3$-KBr solution should be reduced and the analysis repeated. The time allowed for bromination should not be over ten minutes.

This method was tested against known aniline samples and was found to give results accurate to 0.1 percent.

An attempt was made to titrate the Br_2 directly with thiosulfate, but very low and erratic titers were obtained.

SAMPLE CALCULATIONS

Hands & Norman Still:

Three Component System; Single Phase (Residue and Distillate)

Initial Charge: 300 ml. DMA
30 ml. HAc (99.5% Temp. 31°C.
1.15 ml. H_2O

Boiling Point before removal of distillate	126.2°C
Boiling point after removal of distillate	127.8
Average boiling point	127.0
Refractive Index of distillate sample (n_D^{25})	1.4314
Weight of sample	0.702g.

Sample diluted to 100 ml. and 25 ml. aliquots taken for titration with 0.0948N NaOH. Titer = 17.91 ml.

Weight percent acetic acid in distillate:

$$\frac{\text{ml. NaOH x normality NaOH}}{\frac{\text{grams sample x aliquot x 10}}{\text{eq. wt. HAc}}} = \text{Weight percent HAc}$$

$$\frac{17.91 \times 0.0948}{\frac{0.702 \times \frac{1}{4} \times 10}{60.05}} = 58.3\% \text{ HAc}$$

Refer to Fig. 2

HAc = 58.3%, n_D^{25} = 1.4314. The point falls midway between the 30.0% and 25.0% DMA lines. DMA = 27.5%.

On a DMA free Basis:

$$\text{HAc} = \frac{58.3}{100 - 27.5} = 80.4\%, \quad H_2O = \frac{14.2}{100 - 27.5} = 19.6\%.$$

Composition of Residue:

$$\text{HAc} = \text{ml. x density}^{1,2} \times \frac{\%}{100} = 30 \times 1.142 \times 0.995 = 31.10\text{g.}$$

$$\text{DMA} = \text{ml. x density}^{4} = 300 \times 0.947 \qquad = 284 \text{ g.}$$

$$H_2O = \text{ml. x density}^{3} + \text{ml. HAc x } \%H_2O \text{ in HAc x density}$$

$$= 1.15 \times 0.996 + 30 \times 1.142 \times .005 \qquad = 1.31 \text{ g.}$$

Total Weight = 316 g.

Weight percent:

HAc = 31.10/316 = 9.84%
DMA = 284/316 = 89.8%
H_2O = 1.31/316 = 0.414%

On DMA free basis, H_2O = $\frac{0.414}{100-89.8}$ = 4.04% (T).

Composition of residue after correction for removal of distillate sample:

Corrected weight = original weight - weight of distillate sample.

HAc = 31.10 - 0.702 x 0.583	= 30.69
DMA = 284 - 0.702 x 0.275	= 283.8
H_2O = 1.31 - 0.702 x 0.142	= 1.21
Total Weight	= 315.7

Weight percent:

HAc = 30.69/315.7 = 9.77%
DMA = 283.8/315.7 = 89.9 %
H_2O = 1.21/315.7 = 0.383%

On a DMA free basis; H_2O = $\frac{0.383}{100-89.75}$ = 3.80% (T).

Average H_2O in residue = $\frac{4.04 + 3.80}{2}$ = 3.92% (T).

II Three component system; two phases (distillate and residue).

Initial Charge: 50 ml. DMA
25 ml. HAc (99.5%) Temp. 29°C.
425 ml. H_2O

Boiling point; 98.5°C.

Distillate sample is separated into phases at 25°C. and each phase is analyzed separately.

Wt.	H_2O layer	DMA layer	Total
Wt.	4.315g.	0.989g.	5.304g.
n_D^{25}	1.3384	1.5547	

Refer to Fig. 2.

HAc composition for each layer is found by locating the refractive index on the solubility envelope and reading the percent HAc.

Percent HAc by refractive index:

H_2O layer	DMA layer
3.5%	0.5%

Reminder of each phase is reweighed and the percent HAc is checked by titration, with 0.1002N NaOH.

	H_2O layer	DMA layer
Wt. sample	4.216 g.	0.901 g.
Ml. 0.1002 N NaOH for titler	2.42	0.70
Wt. percent HAc	3.50%	0.47%

On Fig. 1, a tie line is drawn between points representing percent HAc in the water layer and percent HAc in the DMA layer which is in equilibrium with the water layer. Length of tie line is 22.2 cm.

The ratio of the weight of the DMA layer to the total weight is:

$$\frac{0.989}{5.304} = 0.186; \quad 0.186 \times 22.2 \text{ cm.} = 4.15 \text{ cm.}$$

4.15 cm. is scaled from the water rich end, and the composition is read:

2.8% HAc, 19.8% DMA, 77.4% H_2O

On a DMA free basis; HAc = 3.5%, H_2O = 96.5% (T).

Liquid composition is calculated in the same manner as in part 1, above.

Note:

DMA = Dimethylaniline
HAc = Acetic acid
H_2O = Water
(T) = Tabulated experimental value

THESIS TITLE: THE EFFECT OF DIMETHYLANILINE ADDITION ON
THE SEPARATION OF ACETIC ACID AND WATER
BY DISTILLATION

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