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THE THREE PHASE SYSTEM
N-HEXANE - ANILINE - WATER

BY

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A THESIS
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ABSTRACT OF THESIS

This is a study of the three phase system - n-Hexane - Aniline - Water at 50° Centigrade. The data obtained, coupled with data previously established at 30° Centigrade is used to predict a means of recovering aniline from 3-5% aqueous solutions by scrubbing with n-hexane.

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EXPERIMENTAL

1. Materials

The n-hexane used was high purity material obtained from Mathieson Company, Inc. It was redistilled through a 24 inch column of 1 inch diameter, packed with 1/8 inch State College Packing. The fraction collected had a boiling point of 155.7°-156.7°F. and a specific gravity of 0.649 at 70°F. This compares with the boiling point of 158°F. and specific gravity of 0.660 at 20°C. found in the literature.¹⁸ It was stored over sodium hydroxide pellets to assure freedom from moisture.

The aniline was high purity material obtained from Mathieson Company, Inc. It was redistilled from zinc dust and carbon black in a 24 inch column, of 1 inch diameter, packed with 1/8 inch State College Packing. The fraction collected had a boiling point of 183° - 184°C. and a specific gravity of 1.012 at 70°F. This compares with the boiling point of 184.4°C. and a specific gravity of 1.0236 at 20°C. found in the literature.¹⁹ It was stored over sodium hydroxide to assure freedom from moisture. The color of the aniline was water white.

The laboratory supply of distilled water was used.

2. Determination of Binary and Ternary Solubilities - Volumetric

The three-phase system solubilities were determined by cloud point procedure whose reliability is affirmed by the reproduceability of results in this investigation, and by Greshes,¹⁷ Seaman, et. al.²⁰ and Sidgwick, et. al.¹²

TABLE 1
EXPERIMENTAL DATA

Binary Systems: (duplicate determinations)

<u>Temperature</u>	<u>ml Water</u>	<u>ml Aniline</u>	<u>ml n-Hexane</u>
50°	20.0	0.05	0.0
50°	20.0	0.80	0.0
50°	20.0	0.80	0.0
50°	1.350	20.0	0.0
50°	1.325	20.0	0.0
50°	1.350	20.0	0.0
50°	0.0	2.45	20.0
50°	0.0	2.40	20.0
50°	0.0	2.40	20.0
50°	0.0	2.40	20.0
50°	0.025	0.0	20.0
50°	0.025	0.0	20.0
50°	20.0	0.0	0.05
50°	20.0	0.0	0.05
50°	0.0	20.0	4.30
50°	0.0	20.0	4.75

TABLE 2

EXPERIMENTAL DATA

Ternary Systems: (duplicate determinations)

A. Water and Aniline; add n-Hexane

<u>Temperature</u>	<u>ml Water</u>	<u>ml Aniline</u>	<u>ml n-Hexane</u>
50°	20.0	0.10	0.30
50°	20.0	0.10	0.25
50°	20.0	0.30	0.25
50°	20.0	0.30	0.30
50°	30.0	1.00	0.30
50°	30.0	1.00	0.35

B. n-Hexane and Aniline; add Water

50°	0.20	0.10	20.0
50°	0.20	0.10	20.0
50°	0.15	0.50	20.0
50°	0.20	0.50	20.0
50°	0.10	1.00	20.0
50°	0.15	1.00	20.0

C. Aniline and Water; add n-Hexane

50°	0.50	20.0	3.9
50°	0.50	20.0	3.8
50°	0.50	20.0	3.2
50°	0.50	20.0	3.2
50°	1.00	20.0	3.0
50°	1.00	20.0	3.0

D. Aniline and n-Hexane; add Water

50°	1.20	20.0	1.0
50°	1.10	20.0	1.0
50°	0.90	20.0	2.0
50°	0.90	20.0	2.0
50°	0.80	20.0	3.0
50°	0.75	20.0	3.0
50°	0.60	20.0	4.0
50°	0.55	20.0	4.0

TABLE 2 (continued)

EXPERIMENTAL DATA

Ternary Systems:

E. Aniline and n-Hexane; add Water (gravimetric - single determinations)

<u>Temperature</u>	<u>Water</u>		<u>Aniline</u>		<u>n-Hexane</u>	
	ml		ml	weight	ml	weight
50°	1.10		20.0	20.2345g.	1.0	0.6721g.
50°	0.85		20.0	20.2391g.	2.0	1.3440g.
50°	0.75		20.0	20.2386g.	3.0	2.0060g.
50°	0.60		20.0	20.2371g.	4.0	2.6876g.

INTRODUCTION

In the manufacture of aniline, the process of separating aniline from water offers considerable difficulty, inconvenience and expense.

The usual method of manufacturing aniline involves the reduction of nitrobenzene with iron filings and hydrochloric acid.* 1,2. The reduction is carried out in a reaction vessel under reflux. The reaction is continued until the reduction is complete. The mixture is steam distilled; and on condensing the vapors an emulsion is obtained which comprises wet aniline and aniline in water. This method, still used by many manufacturers, gives rise to large quantities of aniline water and requires large expenditures and losses in processing. The aniline is removed from the separator and sent to the rectifier for purification and removal of water. The aniline water (4,960 lbs. water containing 3-5% aniline is obtained per 860 lbs. of aniline^{1*}) is treated in varying ways to recover the aniline.^{3,4.} These include, (a) distillation of the aniline which, however, requires large expenditures in steam; (b) extraction with nitrobenzene which is used in the next reduction, but this necessitates a large number of tanks and is in general a cumbersome method; and (c) return of aniline water to the boiler generating steam for use in steam distillation. This last operation, though quite simple, has not found wide application.

A solvent extraction system might be developed which would

* References to the literature are listed on page 20.

effectively and inexpensively recover the aniline from the aniline water. The present investigation was undertaken to obtain additional data on an aniline - n-hexane - water system preliminary to prediction and design of a counterflow liquid-phase separation process for the extraction of aniline water (and from water saturated aniline).

Drucker⁵ determined some liquid-phase equilibrium for the aniline - n-hexane - water system but his interests lay in determining the change in critical solubility temperature and so covered only a small, inadequate fraction of the particular system. Binary solubilities have been recorded for the systems water-aniline^{6,7,8,9,10,11,12}; aniline-n-hexane^{5,13,14} and n-hexane-water.^{15,16}

The following investigation was made to extend the work by Greshes¹⁷ who studied the system aniline - n-hexane - water over a wide concentration range at 36°C. Although extreme care had to be exercised in making binary determinations, his results showed good agreement with data found in the literature. The tie lines obtained by Greshes and in this study were also in good agreement. The extraction ratio found by Greshes for the system at 36°C. was equal to 2:1 and is exactly the same as that found in this study of the system at 50°C. The binary data comparison is shown in Table 11 on page 26.

Four bottles containing the pure components of the system were placed in a constant temperature bath for a few hours prior to running; the cloud point determinations and brought to operating temperature. The bath temperature was maintained within 0.5° of 50°C . by a mercury column thermostat, relay and electric heaters. When running binary mixtures, the primary component was accurately pipetted into a glass-stoppered flask and immersed in the bath until bath temperature had been reached. The secondary component was then titrated slowly from a 10 ml micro-burette and the flask was shaken after each incremental addition and replaced in the bath until operating temperature was again reached. At the first sign of clouding, the titration was stopped and the sample shaken and immersed for 30 minutes to make certain the system was at equilibrium. This was continued until a permanent cloud was obtained. The ternary systems were run in a similar manner except that the two primary components were added in a single phase region, in the flask together and the ternary component was titrated, as described, from the micro-burette.

All runs were in duplicate except for four tests on the aniline and n-hexane plus water system which were measured gravimetrically as checks on the volumetric determinations of solubility in the aniline phase.

The experimental data thus obtained is listed in Tables 1 and 2. In the binary mixtures the primary component has the larger volume (20 - 30 ml). The secondary, titrated, component is in all cases

the lesser amount. The sub-heading of the ternary systems indicate the two primary and ternary components. "Aniline and water; add n-hexane" for example, means the aniline and water are the two primary components and the n-hexane is the titrated, ternary, component.

3. Determination of Three-Phase System Solubilities - Gravimetric

As a check on the reliability of the method and on that phase of the procedure wherein volumetric measure was used to determine percentage concentrations, 4 additional samples were run using weight measurements. Specific volumes of aniline and n-hexane were introduced into tared bottles from a burette and the weight of each component was recorded. Water was then added until the cloud point was reached and the weight of the water recorded. These cloud point determinations compared very favorably with those previously determined by volumetric measurements.

The data which resulted is recorded in Table 2.

4. Determination of Conjugate and Tie Lines.

The tie lines and three-phase conjugate lines were obtained by charging known mixtures of the three components to graduated cylinders, agitating during the course of 12 - 14 hours and then allowing the phases to separate, all in the constant temperature bath. Samples of the individual phases were pipetted, weighed, accurately diluted with methanol and analyzed for aniline by spectrophotometer in the ultraviolet range. Since the aniline concentration locates a point on a phase boundary curve, this figure is used to pick off the remaining percentages of water and hexane from the equilibrium curves represented by Figures 4, 5 and 6. Thus, the entire composition becomes available. The sum of the aniline content of the phases agreed with the quantity of aniline charged.

The aniline analysis was performed on a Beckman Model DU quartz

spectrophotometer at a wave length of 290 mu.²¹ The proper wave length was determined by plotting the percent transmission of a sample containing 0.0020g aniline per 100 ml. of methanol against the wavelengths in the ultraviolet range (Figure 2). The wavelength selected for the calibration (290mu) was that wave length which fell just to the right of the minimum at 285 mu. The spectrophotometer was calibrated at 290 mu between 0.001g./100 ml and 0.003g./100ml.

The experimental data are summarized in Tables 3, 4 and 5 and in Figures 1, 2 and 3. Table 3 describes the calibration of the Beckman spectrophotometer for the aniline analysis. Tables 4 and 5 describe the determination of the three-phase conjugate lines and tie lines respectively. Figures 1 and 3 represent part (a) of Table 3 plotted on semi-log and rectangular coordinate paper. Figure 2 represents part (b) of Table 3.

A sample calculation of the data contained in Tables 3 and 4 follows:

Basis: Data for aniline of sample no. 1, Table 4.

1. Original volume of aniline introduced	10.0 ml.
2. Final volume of aniline at equilibrium	10.0 ml.
3. Aliquot of aniline layer taken for analysis	5.0 ml.
4. Weight of 5 ml. aliquot	4.2810 ml.

5. Dilutions of 5 ml. aliquot:
- a. 5 ml aliquot diluted to 100 ml. with methanol.
 - b. 5 ml of mixture a diluted to 100 ml with methanol.
 - c. 5 ml of mixture b diluted to 100 ml with methanol.
 - d. 5 ml of mixture c diluted to 100 ml with methanol.
6. Spectrophotometer reading of sample 5d. 70.0%
transmission.

TABLE 3

EXPERIMENTAL DATA

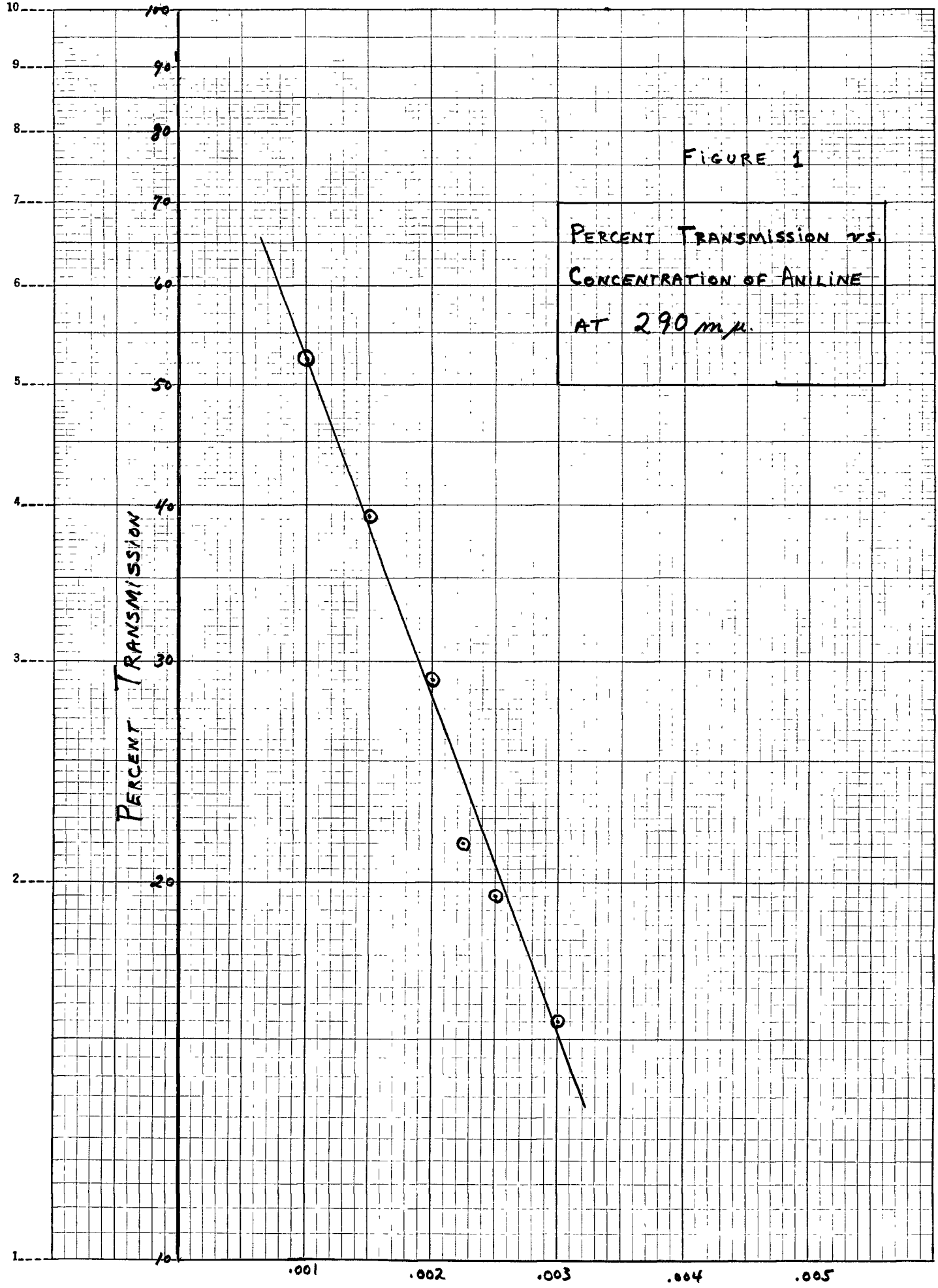
Beckman Spectrophotometer Calibration

A. Calibration at 290 mμ (Figure 1 and Figure 3).

<u>Concentration g/100 ml.</u>	<u>% Transmission</u>
0.00100	52.5
0.00150	31.5
0.00200	28.0
0.00225	23.0
0.00250	19.0
0.00300	16.0

B. Determination of Wavelength (concentration = 0.00200 g/100ml)
(Figure 2)

<u>Wavelength</u>	<u>% Transmission</u>
215	0.5
218	6.5
220	5.1
225	2.5
230	1.0
240	1.0
243	2.0
247	5.2
249	6.0
250	10.5
255	27.0
260	37.5
265	36.5
270	31.0
275	26.2
280	23.5
285	24.0
290	20.0
300	50.0
310	62.0
330	98.5



CONCENTRATION - GM./100 ML.

FIGURE 2

PERCENT TRANSMISSION VS. WAVELENGTH

ANILINE IN METHANOL = .002 CM./100ML.

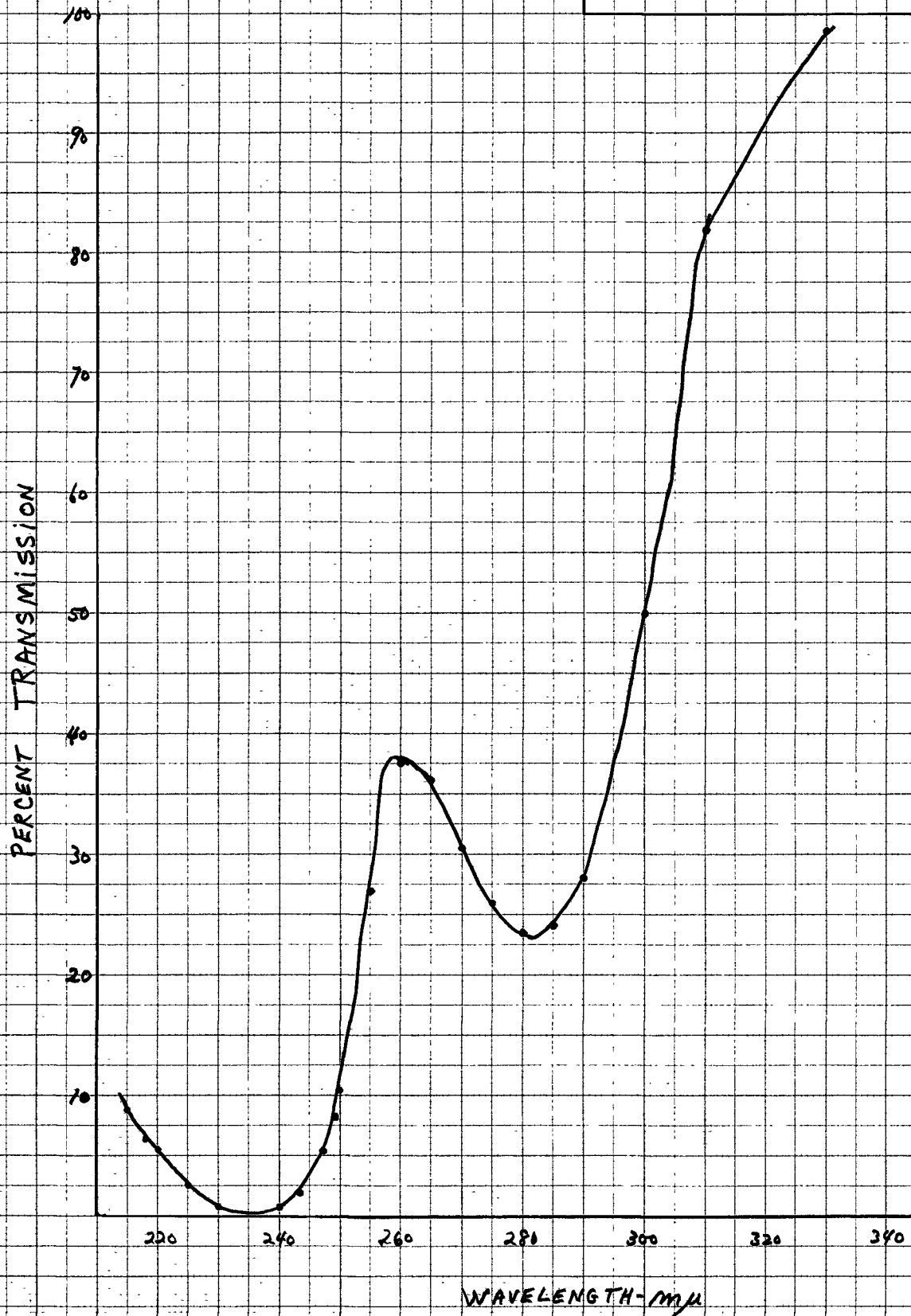


FIGURE 3

PERCENT TRANSMISSION
VS. CONCENTRATION OF
ANILINE AT 290 mμ.

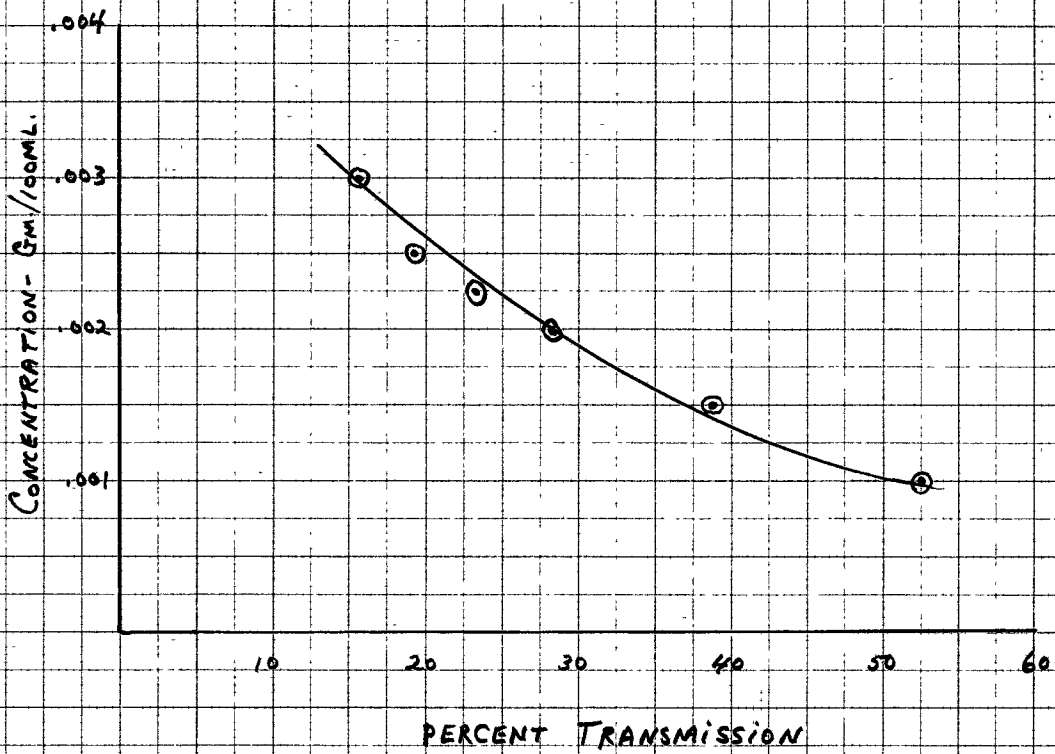


TABLE 4

EXPERIMENTAL DATA

Three Phase Line Data

1. Original Volumes of Material Introduced.

<u>Sample No.</u>	<u>ml Water</u>	<u>ml Aniline</u>	<u>ml n-Hexane</u>
1.	10.0	10.0	10.0
2.	10.0	10.0	20.0
3.	10.0	10.0	30.0
4.	20.0	10.0	10.0
5.	10.0	10.0	20.0
6.	20.0	10.0	10.0

2. Final Volumes at Equilibrium

1.	10.0	10.0	10.0
2.	10.0	10.0	20.0
3.	10.0	9.0	31.0
4.	20.0	9.0	11.0
5.	10.0	9.0	21.0
6.	20.5	9.5	10.0

3. Weights of 5 ml. Aliquots at Equilibrium Used for Analysis
of Aniline

1.	5.2025	4.3810	3.2400
2.	5.1066	4.9635	3.2196
3.	5.0081	4.9891	3.2580
4.	5.1360	4.9606	3.2404
5.	5.0948	4.9814	3.2401
6.	5.1012	5.0374	3.2544

4. Dilutions of Each Sample in 3 above

<u>Sample</u>	<u>Total Dilution</u>
(1) Hexane	1/8000
(1) Aniline	1/160,000
(1) Water	1/8000
(2) Hexane	1/8000
(2) Aniline	1/160,000
(2) Water	1/8000

TABLE 4 (Continued)

EXPERIMENTAL DATA

4. Dilutions of Each Sample in 3 above

<u>Sample</u>	<u>Total Dilution</u>
(3) Hexane	1/8000
(3) Aniline	1/160,000
(3) Water	1/8000
(4) Hexane	1/8000
(4) Aniline	1/160,000
(4) Water	1/8000
(5) Hexane	1/8000
(5) Aniline	1/160,000
(5) Water	1/8000
(6) Hexane	1/8000
(6) Aniline	1/160,000
(6) Water	1/8000

5. Spectrophotometer Reading of Last Diluted Sample Above

<u>Sample No.</u>	<u>% Transmission</u> <u>Hexane Layer</u>	<u>% Transmission</u> <u>Aniline Layer</u>	<u>% Transmission</u> <u>Water Layer</u>
1.	72.0	70.0	72.0
2.	62.0	70.5	72.0
3.	55.0	70.5	84.0
4.	73.0	69.5	73.0
5.	59.5	70.5	75.0
6.	72.5	69.0	73.5

TABLE 5
EXPERIMENTAL DATA

Tie Lines

1. Original Volumes of Material Introduced.

<u>Sample No.</u>	<u>ml. Water</u>	<u>ml. Aniline</u>	<u>ml. n-Hexane</u>
1.	20.0	0.50	20.0
2.	15.0	2.00	30.0

2. Final Volumes at Equilibrium

1.	20.25	---	20.25
2.	16.00	---	31.00

3. Weight of 5 ml Aliquots at Equilibrium used for Analysis of Aniline

1.	5.0254	---	3.2491
2.	5.1042	---	3.2405

4. Dilutions of Each Sample in 3 Above

<u>Sample</u>	<u>Total Dilution</u>
1. n-Hexane	3/2000
1. Water	3/2000
2. n-Hexane	3/20,000
2. Water	3/20,000

5. Spectrophotometer Reading of Last Diluted Sample Above

<u>Sample</u>	<u>% Transmission</u> <u>Hexane Layer</u>	<u>% Transmission</u> <u>Water Layer</u>
1.	29.0	46.0
2.	57.0	73.5

RESULTS

1. Three-Phase System Solubilities

The results of the three-phase solubilities of the n-hexane - aniline - water system at 50°C. are summarized in Tables 6, 7 and 8 and in Figures 4, 5, 6 and 7. The data of Tables 6, 7 and 8 are represented in Figures 4, 5 and 6 respectively, and these represent the water, n-hexane and aniline phases respectively. All three plots are on the same scale. Figure 7 contains a composite of all three systems on a small scale.

A sample calculation of the data contained in these tables follows:

Basis: Data for percent water, aniline and n-hexane in the water phase of sample no. 2, Table 6.

1. Volume of n-hexane (from Table 1)	0.3 ml.
2. Specific gravity of n-hexane (from Table 2)	0.649g/ml.
3. Weight of n-hexane (0.3 x 0.649)	0.19g.
4. Volume of aniline (from Table 1)	0.1 ml.
5. Specific gravity of aniline (from Table 2)	1.012g/ml.
6. Weight of aniline (0.1 x 1.012)	0.10g.
7. Volume of water (from Table 1)	20.0 ml.
8. Specific gravity of water (from Table 2)	1.00g/ml.
9. Weight of water (20.0 x 1.00)	20.00g.
10. Total weight of sample:	

n-hexane	0.19
aniline	0.10
water	20.00
	<u>20.29</u>

11. Weight percent n-hexane (0.18/20.29)	0.9%
12. Weight percent aniline (0.10/20.29)	0.5%
13. Weight percent water (20.0/20.29)	98.6%

TABLE 6

WEIGHT PERCENTAGES OF THE VARIOUS COMPONENTS AT EQUILIBRIUM

(duplicate determinations)

Water Phase - Weight %

<u>Water</u>	<u>Aniline</u>	<u>n-Hexane</u>
96.1	3.9	0.0
96.1	3.9	0.0
98.6	0.5	0.9
98.6	0.5	0.9
97.7	1.5	0.8
97.7	1.5	0.8
96.1	3.2	0.7
96.1	3.2	0.7
99.8	0.0	0.2
99.8	0.0	0.2

FIGURE 4

GRAPHIC REPRESENTATION OF
EQUILIBRIUM DATA - WATER
PHASE.
—— THREE PHASE LINE
- - - - TIE LINE

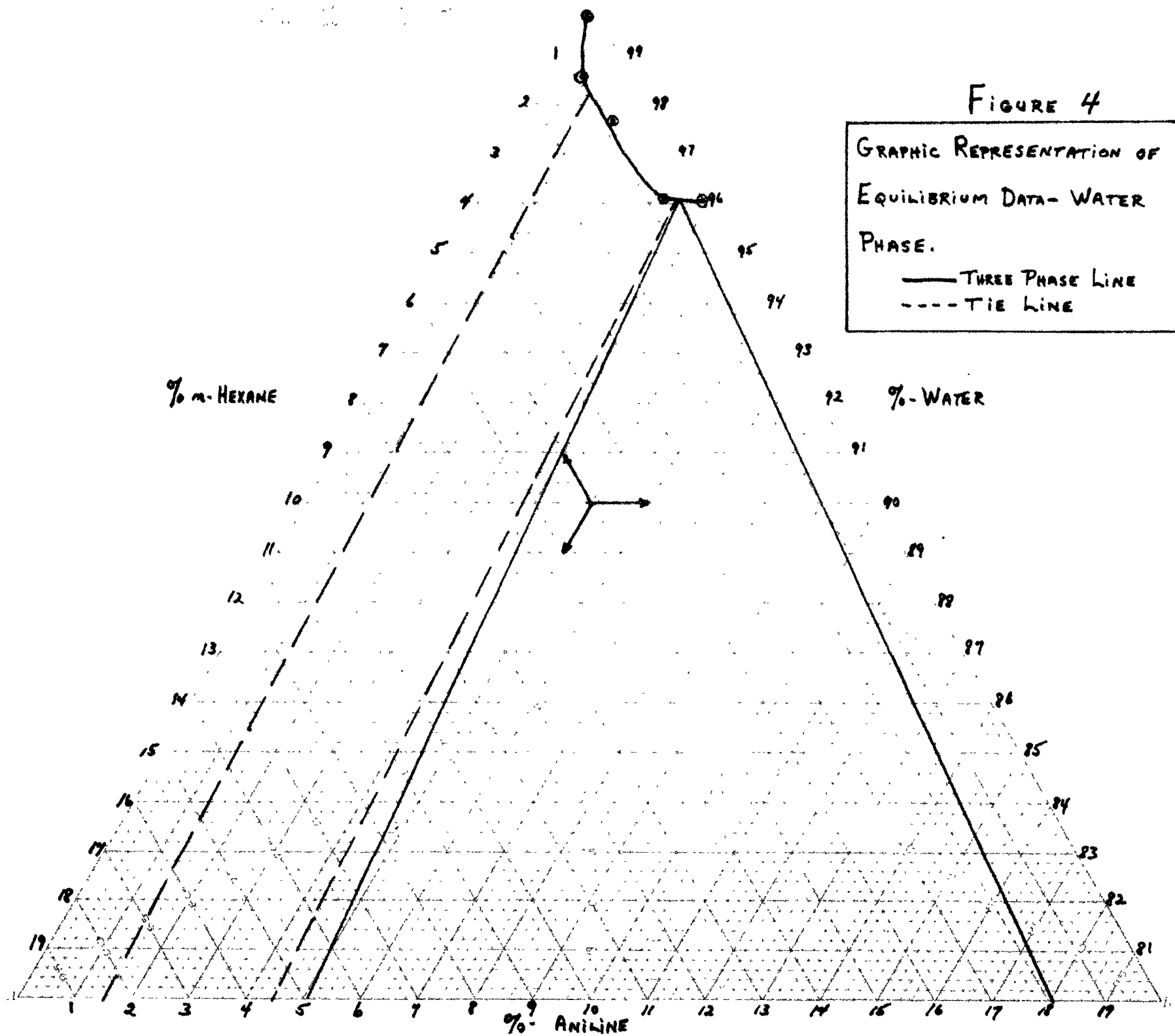


TABLE 7

WEIGHT PERCENTAGES OF THE VARIOUS COMPONENTS AT EQUILIBRIUM

(duplicate determinations)

Hexane Phase - Weight %

<u>Water</u>	<u>Aniline</u>	<u>n-hexane</u>
0.5	0.0	99.5
0.5	0.0	99.5
1.5	0.3	97.7
1.5	0.3	97.7
1.1	3.3	95.1
1.1	3.	95.1
0.7	7.2	92.1
0.7	7.2	92.1
0.0	16.0	84.0
0.0	16.0	84.0

FIGURE 5

GRAPHIC REPRESENTATION OF
EQUILIBRIUM DATA - HEXANE
PHASE.
— THREE PHASE LINE
- - - TIE LINE

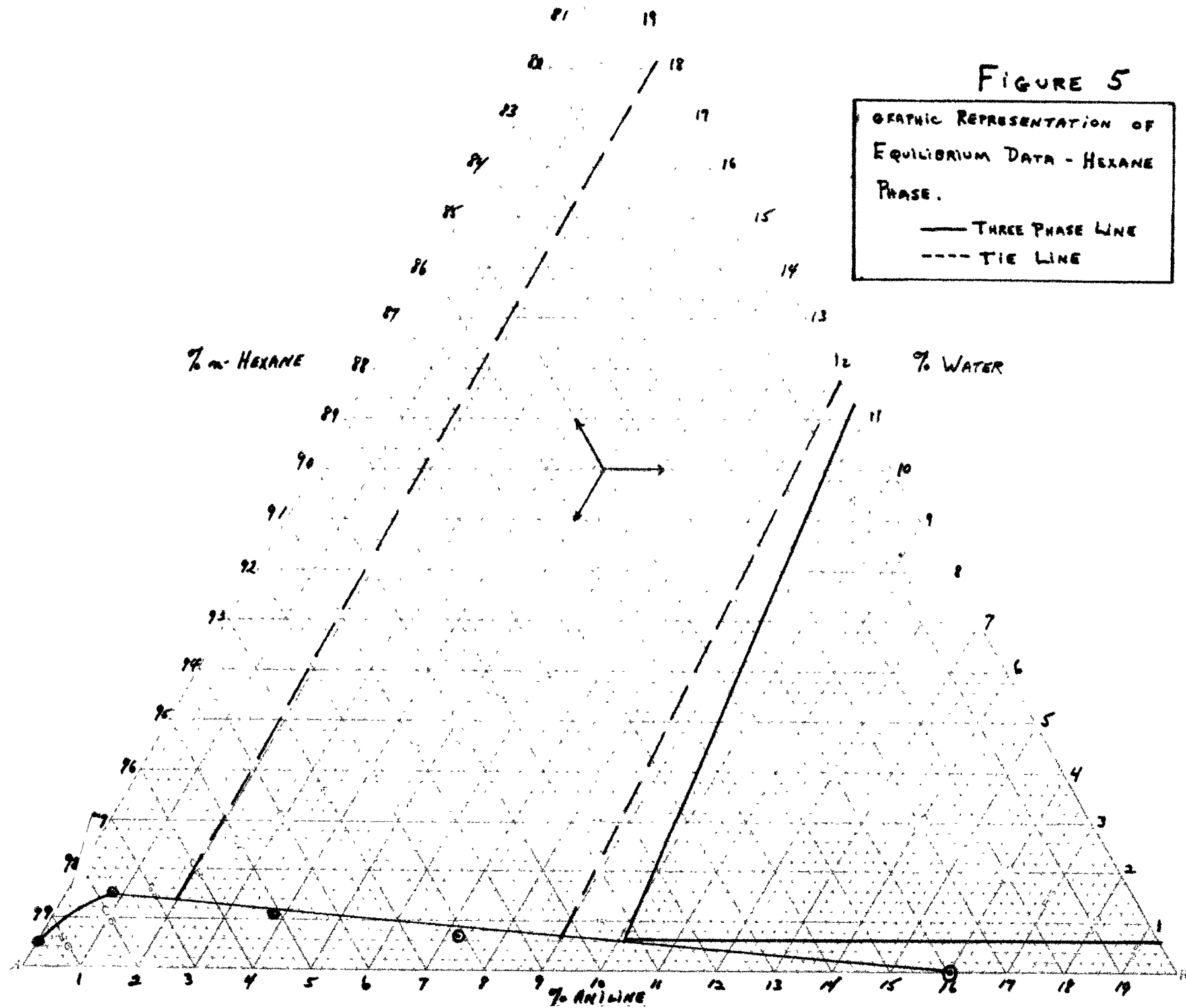


TABLE 8

WEIGHT PERCENTAGES OF THE VARIOUS COMPONENTS AT EQUILIBRIUM

(duplicate determinations)

Aniline Phase - Weight %

<u>Water</u>	<u>Aniline</u>	<u>n-Hexane</u>
6.3	23.7	0.0
6.3	23.7	0.0
2.2	37.2	10.6
2.2	37.2	10.6
3.5	37.6	8.9
3.5	37.6	8.9
4.3	37.3	8.4
4.3	37.3	8.4
4.1	91.7	4.2
4.1	91.7	4.2
3.7	90.2	6.1
3.7	90.2	6.1
3.2	38.4	6.4
3.2	38.4	6.4
2.3	36.5	11.2
2.3	36.5	11.2
0.0	36.6	13.4
0.0	36.6	13.4

The 4 samples determined gravimetrically follow:

(single determinations)

4.0	92.1	3.9
3.6	90.6	5.8
3.5	37.7	8.9
2.5	36.1	11.4

FIGURE 6

GRAPHIC REPRESENTATION OF
EQUILIBRIUM DATA - ANILINE
PHASE.

- - VOLUMETRIC RESULTS
- △ - GRAVIMETRIC RESULTS
- THREE PHASE LINE

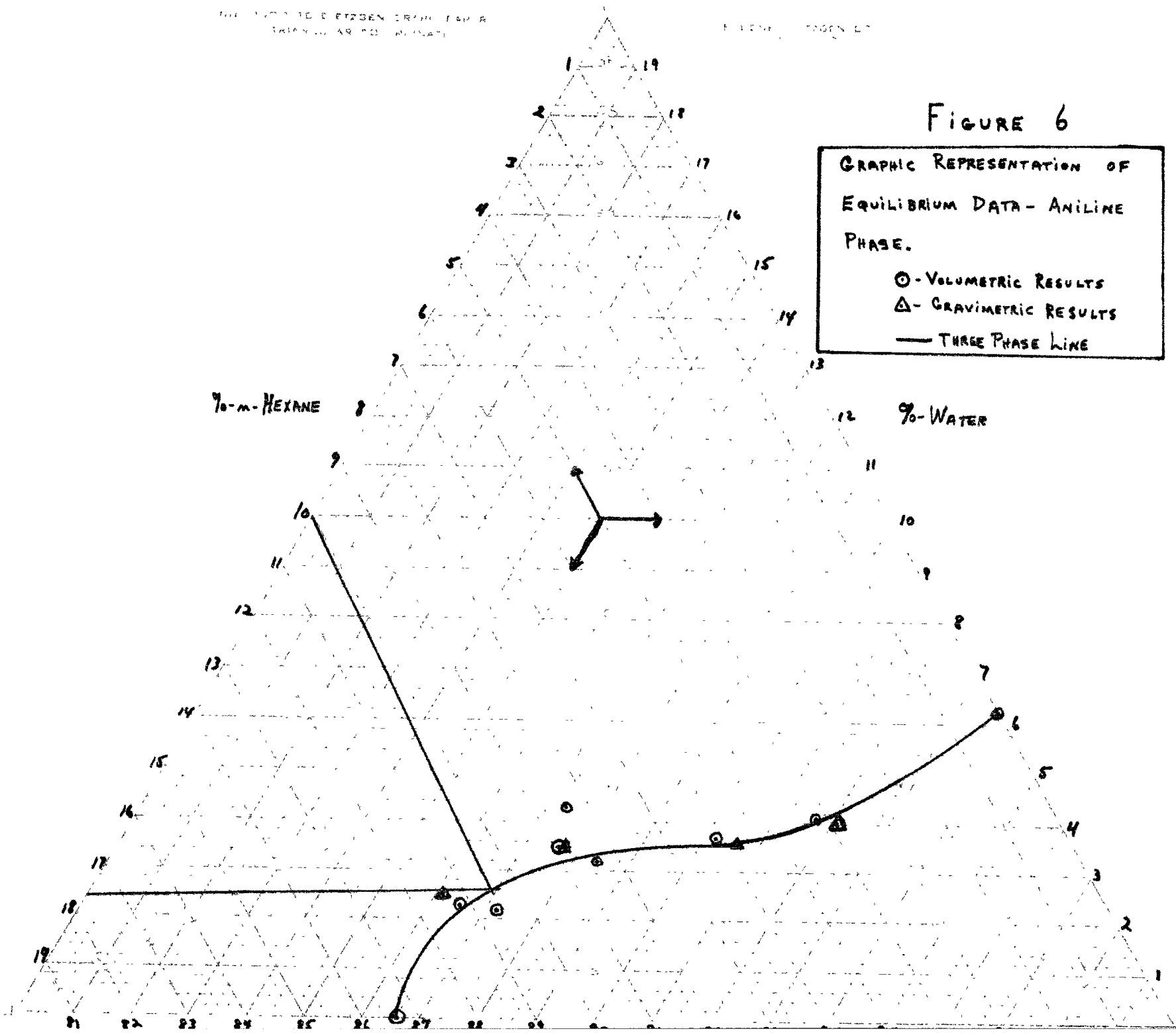


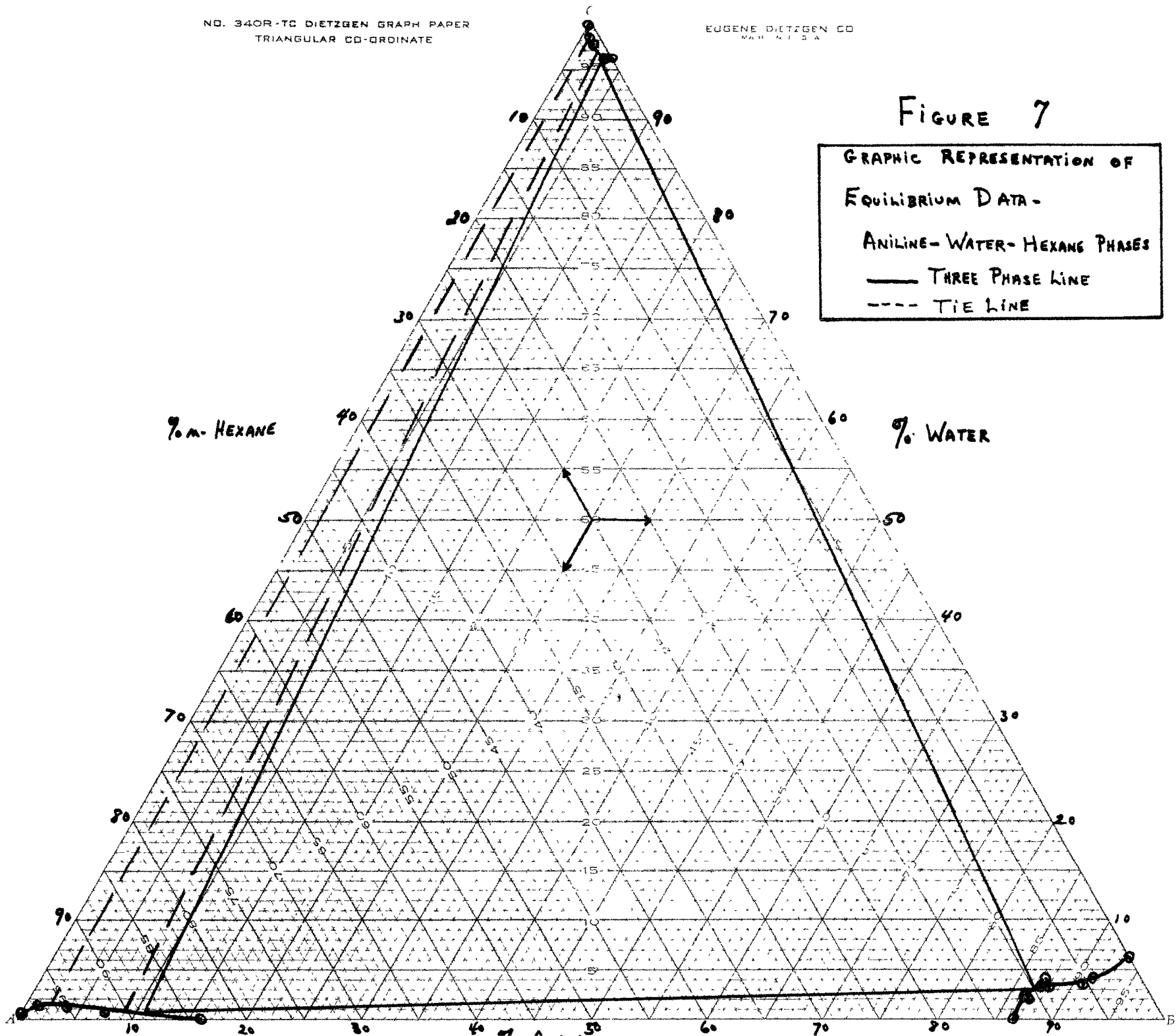
FIGURE 7

GRAPHIC REPRESENTATION OF
EQUILIBRIUM DATA -

ANILINE-WATER-HEXANE PHASES

— THREE PHASE LINE

- - - TIE LINE



2. Three-Phase Conjugate and Tie Lines

Tables 9 and 10 show the aniline concentration and composition of the various phases at equilibrium of the tie lines and conjugate lines. The conjugate and tie lines are represented in Figures 4, 5, 6 and 7.

The results of Table 10 are obtained by picking off the composition of each phase from the trilinear phase diagrams (Figures 4, 5 and 6) knowing the percent aniline (Column 6, Table 9).

A sample calculation of the results obtained in Table 9 follows:

Basis: Data for n-hexane phase of sample no. 1 of conjugate line, Table 9.

- | | |
|---|----------------|
| 1. Original volume of n-hexane introduced
(From Table 4) | 10.0ml. |
| 2. Final volume of n-hexane at equilibrium
(From Table 4) | 10.0ml. |
| 3. Aliquot of n-hexane layer taken for analysis
(From Table 4) | 5.0ml. |
| 4. Weight of 5 ml aliquot (From Table 4) | 3.2400g. |
| 5. Dilution of 5 ml aliquot (From Table 4) | |
| a. 5 ml aliquot diluted to 100 ml with methanol. | |
| b. 5 ml of solution <u>a</u> diluted to 100 ml with methanol. | |
| c. 5 ml of solution <u>b</u> diluted to 100 ml with methanol. | |
| 6.. Spectrophotometer reading of diluted solution <u>5c</u>
(From Table 4) | 72.0% |
| 7. Concentration of aniline in diluted solution <u>5c</u>
as determined from Figure 1. | 0.0005g/100ml. |

8. Concentration of aniline in diluted solution 5b
($0.0005 \times 100/5$) 0.01g/100 ml.
9. Concentration of aniline in diluted solution 5a
($0.010 \times 100/5$) 0.20g/100ml
10. Weight of aniline in the 5 ml aliquot (same as
total aniline in solution 5a). 0.20g/5ml
11. Weight of aniline in the total 10 ml of the
n-hexane phase. (0.20×2) 0.40g
12. Percent of aniline in the n-hexane phase
($0.20\text{g aniline}/5 \text{ ml}$) / ($3.2400\text{g. total}/5 \text{ ml}$) 6.2%

TABLE 9

CALCULATED DATATHREE CO-JUGATE PHASE LINEDetermination of Aniline Concentration

<u>Sample no.</u>	<u>Component</u>	<u>Concentration from Calibration Curve (Figure 1)</u>	<u>Amount in 5 ml of Phase</u>	<u>Total in Phase</u>	<u>% Composition in Phase</u>
1.	n-hexane	0.00050	0.20	0.40	6.2
	aniline	0.00055	4.40	8.80	90.0
	water	0.00050	0.20	0.40	3.8
2.	n-hexane	0.00075	0.30	1.20	9.2
	aniline	0.00054	4.32	8.64	87.0
	water	0.00050	0.20	0.40	3.8
3.	n-hexane	0.00092	0.37	2.29	11.3
	aniline	0.00054	4.32	7.78	86.7
	water	0.00025	0.10	0.20	2.0
4.	n-hexane	0.00048	0.19	0.42	5.9
	aniline	0.00056	4.48	8.06	90.4
	water	0.00043	0.19	0.76	3.7
5.	n-hexane	0.00080	0.32	1.34	9.9
	aniline	0.00054	4.32	7.78	86.8
	water	0.00043	0.17	0.34	3.3
6.	n-hexane	0.00049	0.19	0.38	6.0
	aniline	0.00057	4.56	8.65	90.4
	water	0.00046	0.18	0.76	3.6

TIE LINES

1.	n-hexane	0.00195	0.065	0.26	2.0
	water	0.00120	0.40	0.162	0.8
2.	n-hexane	0.00088	0.290	1.00	9.0
	water	0.00046	0.180	0.57	3.5

TABLE 10

CALCULATED DATA

THREE CONJUGATE PHASE LINE

Phase Composition At Equilibrium

Aniline Phase - Weight %

<u>Aniline</u>	<u>Water</u>	<u>n-Hexane</u>
90.0	3.6	6.4
87.0	2.8	10.2
86.7	2.5	10.8
90.4	3.6	6.0
86.8	2.6	10.6
90.4	3.6	6.0

Water Phase - Weight %

3.8	96.0	0.2
3.8	96.0	0.2
2.0	97.1	0.9
3.7	96.0	0.3
3.3	96.1	0.6
3.6	96.0	0.4

n-Hexane - Weight %

6.2	0.9	92.9
9.2	0.6	90.2
11.3	0.4	88.3
5.9	0.9	93.2
9.9	0.5	89.6
6.0	0.9	93.1

TIE LINES

Water Phase - weight %

0.8	98.4	0.8
3.5	96.1	0.4

n-Hexane Phase - Weight %

2.0	1.3	96.7
9.0	0.6	90.4

3. Conclusions

a. Accuracy of measurements

The same difficulties were encountered in making cloud point determinations as those experienced by Greshes,¹⁷. The cloud points differed in each phase and only in the aniline phase, upon the addition of n-hexane, did a true cloud point appear. All other cloud point determinations were recorded as the first droplet of the introduced material which floated or settled to the bottom, as the case might be. Although this required a careful and tedious technique, accurate cloud points were obtained which could be duplicated.

The binary data compare favorably with the equivalent data found in the literature.^{11, 12, 14}. This is shown by Table 11.

The three phase conjugate lines compare favorably with one another. The tie-lines agree well with the expected results.^{17, 22}.

b. Distribution data and curve

These data are represented by Figure 3 which is a graphic representation of the tie lines and three phase line data of Table 10. From the slope of the line and the distribution of aniline between n-hexane and water, the relative volume ratio of water to n-hexane for completely scrubbing a 3% aniline in water solution is found to be 1 in 2 at 50°C. plus or minus 0.5°C. Significantly, this is the same extraction ratio as that determined by Greshes,¹⁷ for this system at 36°C. as shown by Figure 3.

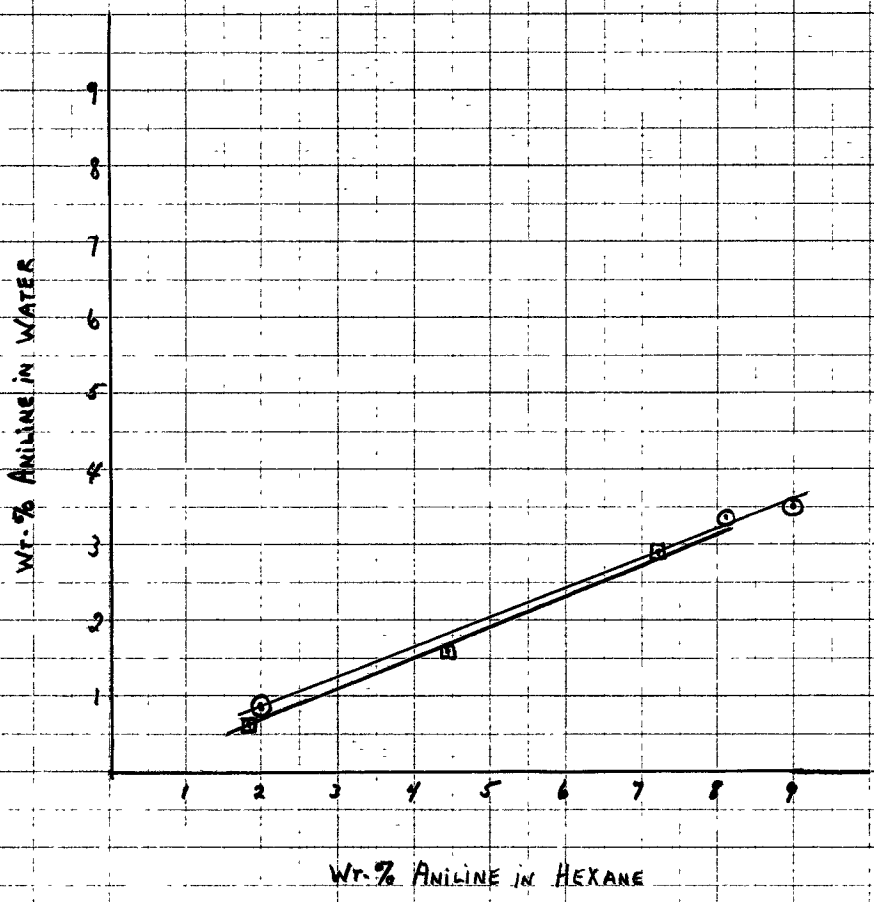
TABLE 11

BINARY DATA COMPARISON

	<u>50°C.</u>		<u>36°C.</u>	
	<u>Weight % Aniline</u>	<u>Weight % Water</u>	<u>Weight % Aniline</u>	<u>Weight % Water</u>
Potosnak	3.9 93.7	96.1 6.3	---	---
Greshes ^{17.}	---	---	3.5 94.4	96.5 5.6
Cambell ^{11.}	4.1	95.9	---	---
Sidgwick ^{12.}	4.1 93.6	95.9 6.4	3.9 94.3	96.1 5.7
	<u>Weight % Aniline</u>	<u>Weight % n-Hexane</u>	<u>Weight % Aniline</u>	<u>Weight % n-Hexane</u>
Potosnak	16.0 88.6	84.0 11.4	---	---
Greshes ^{17.}	---	---	11.0 90.0	89.0 10.0
Keyes ^{14.}	18.0 86.0	82.0 14.0	11.0 88.0	89.0 12.0

FIGURE 8

DISTRIBUTION OF ANILINE
BETWEEN m-HEXANE AND WATER.
○ - AT 50°C
□ - AT 36°C



c. Application

Using the accumulated data we can now define a method for extracting the aniline from a 3-5% water solution. The information in Table 10 is plotted in Figure 9 on an expanded scale. Using this plot, a graphical solution can be used to determine the number of equilibrium stages required. The graphical solution is given by Figure 10.

Basis:

$$X_0 = \text{feed} = 0.04 \qquad X_n = \text{final raffinate} = 0.008$$

$$Y_n \text{ plus } 1 = \text{solvent} = 0.005 \qquad Y_1 = \text{final extract} = 0.06$$

Solvent to feed ratio is 2:1; therefore, 2 pounds of n-hexane are required to extract 1 pound of aniline-water. This determines the line $X_n J_x Y_1$, since $X_n J_x : J_x Y_1 :: 2:1$. Hence, $X_n J_x = 6.3$, $J_x Y_1 = 3.15$ and thus, Y_1 is found to be 0.06. The intersection of the lines through $X_n Y_n$ plus 1, and $X_0 Y_1$ determines the point.

	<u>Mass Fraction Aniline in Extract</u>	<u>Mass Fraction Aniline in Raffinate</u>
	<u>Y</u>	<u>X</u>
1.	0.06	0.016
2.	0.025	0.0084
3.	0.015	0.0077

The extraction would be carried out in countercurrent fashion similar to that in Figure 11. The final extract could be chilled to around 0°C, where aniline and hexane would separate completely. The n-hexane removed would be recycled as shown. The extract temperature required to effect this separation remains to be determined from a study of this system at or near 0°C.

FIGURE 9

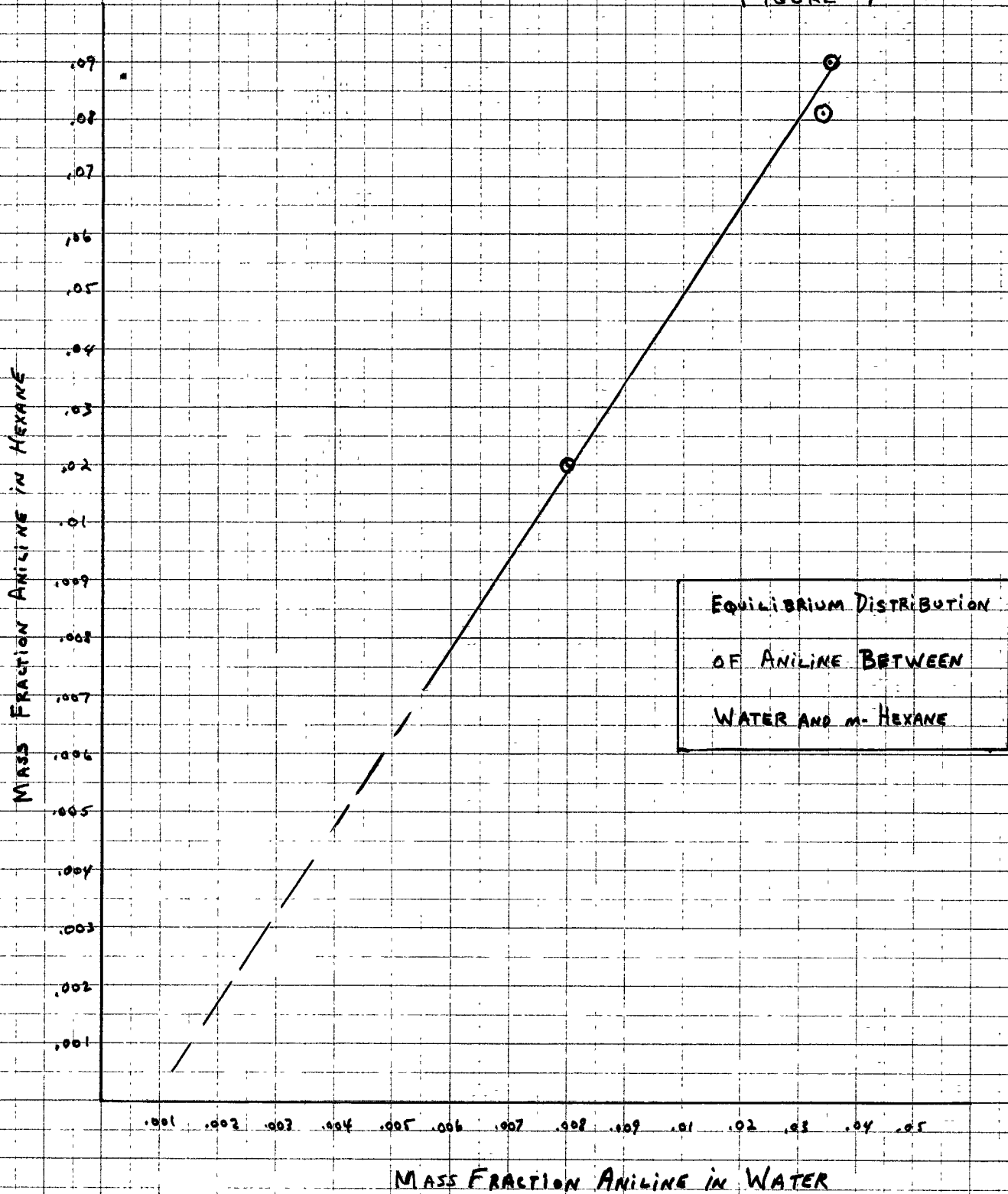
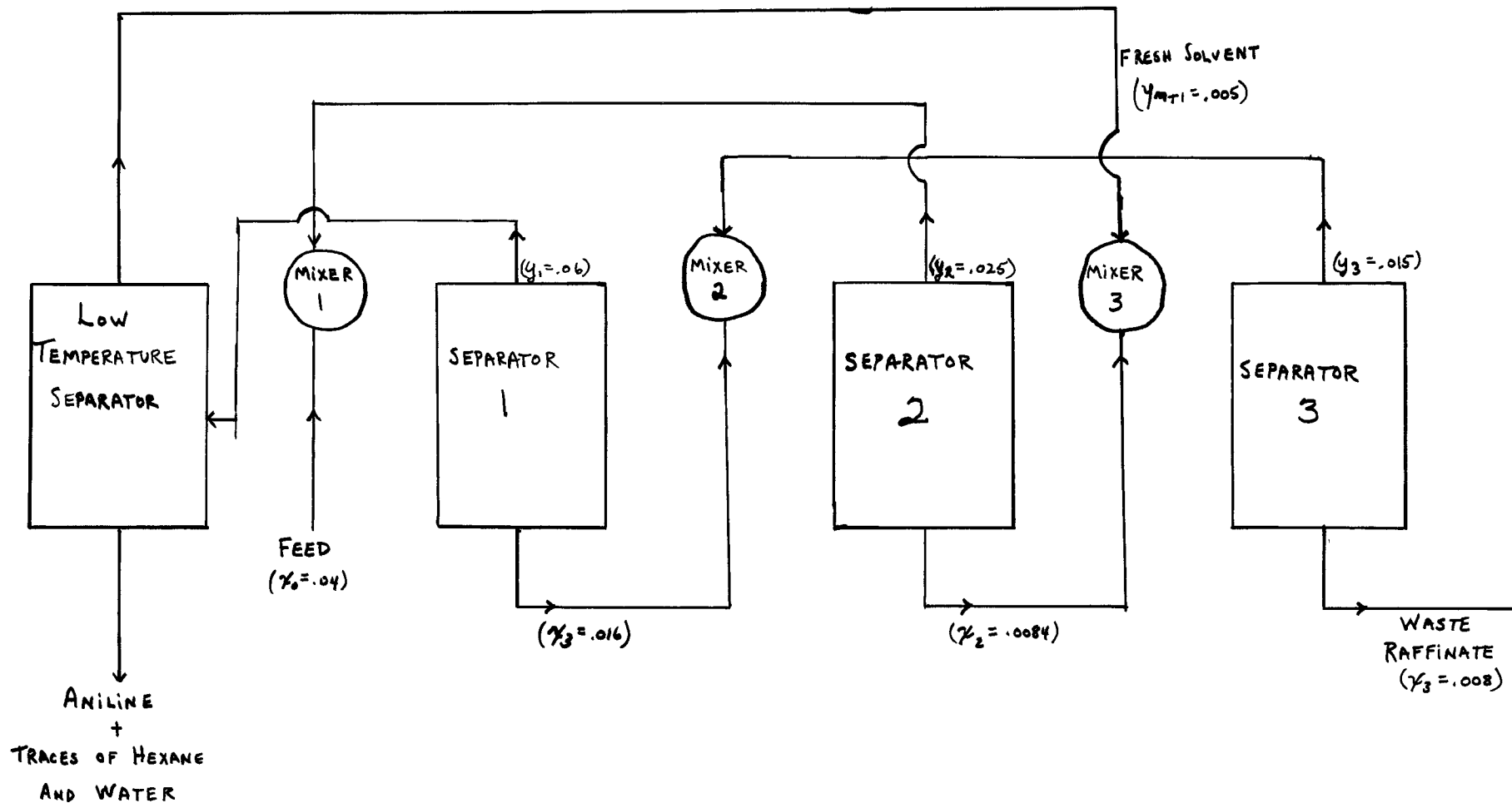


FIGURE 11



THREE STAGE COUNTER CURRENT
EXTRACTION SYSTEM FOR
REMOVING ANILINE FROM
WATER WITH HEXANE

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