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Continuous chlorosulfonation of benzene II phase relations

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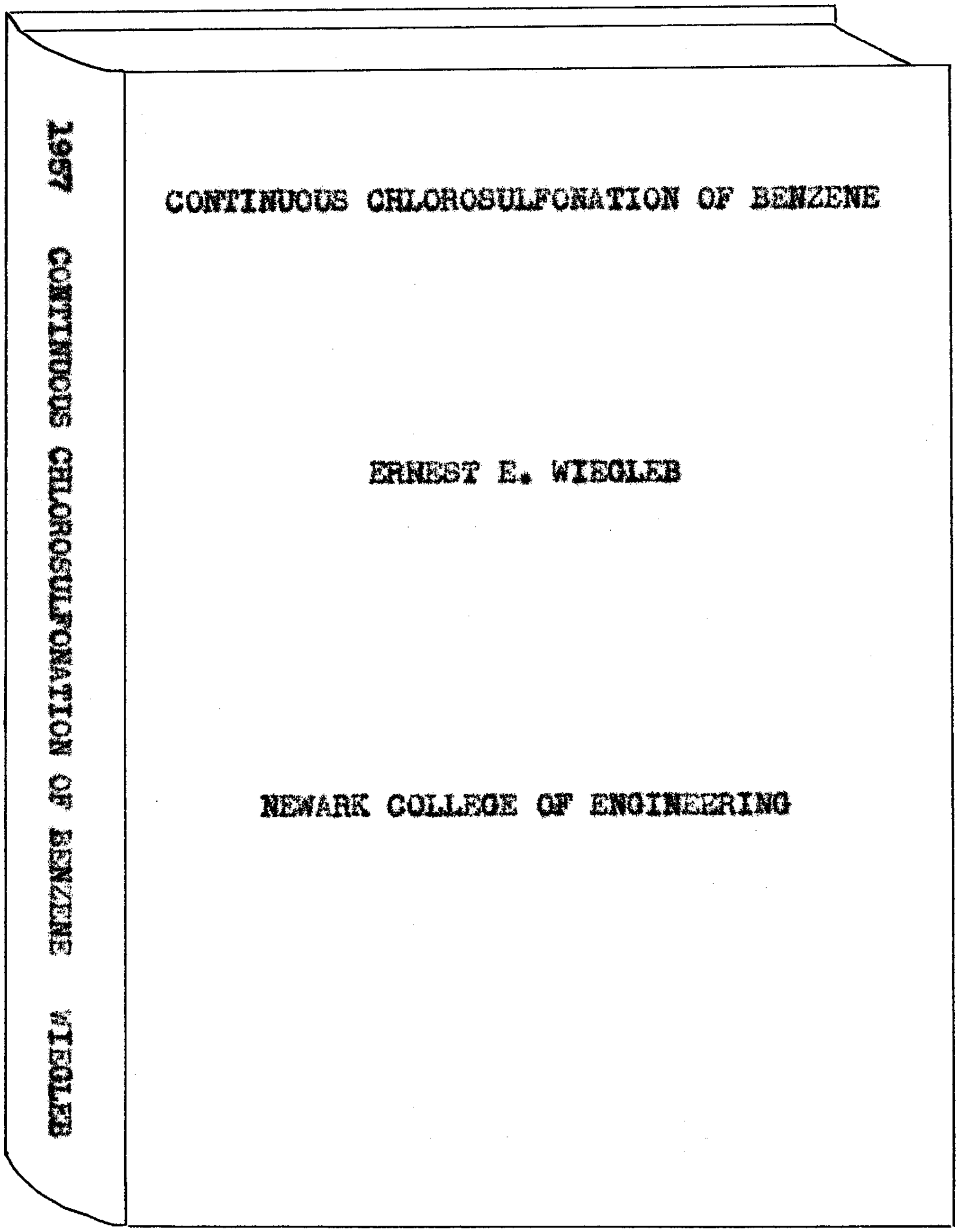
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WIEGLEB
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CONTINUOUS CHLOROSULFONATION OF BENZENE

II PHASE RELATIONS

BY

ERNEST E. WIEGLEB

A THESIS
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ABSTRACT

This work presents data for the separation of materials involved in the chlorosulfonation of benzene using carbon tetrachloride as an inert extraction solvent. Equilibrium and tie line data for the liquid ternary systems; carbon tetrachloride - chlorosulfonic acid - sulfuric acid; benzenesulfonyl chloride - carbon tetrachloride - sulfuric acid; benzenesulfonyl chloride - chlorosulfonic acid - sulfuric acid and for the quaternary system benzenesulfonyl chloride - carbon tetrachloride - chlorosulfonic acid - sulfuric acid have been determined. The tie line data has been correlated by the method of Othmer and Tobias.

Data for two chlorosulfonations made under differing conditions is also given.

APPROVAL OF THESIS

FOR

DEPARTMENT OF CHEMICAL ENGINEERING
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BY

FACULTY COMMITTEE

APPROVED: ______________________

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INTRODUCTION

Chlorosulfonation is used industrially in the preparation of chemical intermediates in the manufacture of dyes and drugs. Commercial practice is to use batch reactions for this process. This work is an attempt to further the knowledge needed to develop a continuous chlorosulfonation process.

The basic reaction involved in chlorosulfonation may be expressed

$$R\cdot H + 2\ ClSO_3H \rightarrow R'SO_2Cl + H_2SO_4 + HCl$$

Some of the possible side reactions may be expressed

$$R\cdot H + ClSO_3H \rightarrow R'SO_3H + HCl$$

$$R'H + R'SO_2Cl \rightarrow R'SO_2\cdot R + HCl$$

$$2\ R'H + H_2SO_4 \rightarrow R\cdot SO_2'R + 2\ H_2O$$

In the batch process large excesses of chlorosulfonic acid are used to drive the reaction to completion and to inhibit the formation of by products. In present practice this valuable raw material is lost for reuse when it is converted to other products during the purification of the sulfonyl chloride.

A continuous chlorosulfonation process in which stoichiometric amounts of the raw materials can be used or in which the unreacted raw materials can be used or in which the unreacted materials can be recovered for reuse would be attractive commercially.

This work is an amplification and continuation of earlier work on this problem (9). Lange in his investigations into the reaction had chosen benzene as the organic reactant because of the availability of information and the simplicity of its reaction with chlorosulfonic acid. The reaction was to be carried out with an inert solvent present which would help drive it to completion by extracting the product from the acid medium as it was formed. Carbon tetrachloride was chosen as the extraction solvent because it possesses the necessary physical and chemical properties and is readily available.

Lange's work had progressed to the point of having completed several exploratory reactions and determining some of the data for the quaternary system benzene sulfonyl chloride - carbon tetrachloride - carbon tetrachloride - chlorosulfonic acid - sulfuric acid including several of the ternary systems involved.

EXPERIMENTAL METHODS

Equilibrium Data

Equilibrium data was obtained by the cloud point method. Known one-phase mixtures of two components were made up and titrated with the third component while being stirred until a second phase or cloudiness appeared. The weight of each component was obtained from the weight increase of the mixture because of the addition.

Tie Line Data

Tie line data was obtained by making up three-component mixtures which would separate into two phases. The phases were allowed to separate into layers. The weights of the two separated layers were obtained. The separated layers were then analyzed for their various components.

Analysis for Sulfuric Acid

The layer to be analyzed was extracted with a known weight of water. The layers from the extraction were separated and weighed. An aliquot of the water layer was titrated with standard sodium hydroxide solution to a phenolphthalein end point. The weight of sulfuric acid in the layer was determined by the use of simultaneous equations involving weight change of the layers in the water extraction and the acidity of the water layer.

Sulfuric Acid (continued)

$$\text{gm. } \phi SO_2Cl + \text{gm. } H_2SO_4 = \text{weight change of layer}$$

$$\frac{\text{gm. } \phi SO_2Cl}{\text{eq. wt. } \phi SO_2Cl} + \frac{\text{gm. } H_2SO_4}{\text{eq. wt. } H_2SO_4} = \text{equivalents in layer}$$

Checks were made on the sulfuric acid determinations by precipitating with barium chloride from a weighed aliquot of the water extraction layer and weighing the ashed precipitate to determine the total sulfate present in the sample. These methods are not applicable when chlorosulfonic acid is present.

Analysis for Carbon Tetrachloride

The organic layer from the water extraction of the sample was weighed and then distilled in a one plate column until the overhead temperature began to rise sharply above 100°C. The distillation flask was then cooled and weighed. The difference in weight from the original distillation sample was taken as the weight of carbon tetrachloride in the layer.

Analysis for Benzenesulfonyl Chloride

The acidity in the water extraction layer unaccounted for by the sulfuric acid previously determined was assumed to be due to benzenesulfonyl chloride which had hydrolyzed during the extraction. The residue from the distillation

<u>Benzenesulfonyl Chloride</u> (continued)

of the solvent layer gave the amount present in that layer. The sum of the quantities in each layer gave the amount of benzenesulfonyl chloride present in the sample.

Sample Calculation

Run 32 Acid Layer

acid layer	23.0 gm.
water added	59.0
solvent layer	4.6
water layer	76.0

Solvent layer distillation

sample	4.6
stripped	3.1
CCl_4	1.5
$\text{Ø}SO_2Cl$	3.1

Water layer neutralization

15.9 ml. of 0.878 N. sodium hydroxide neutralized a 2.9449 gm. aliquot of the water layer.

$$15.9 \text{ ml.} \times 0.878 \text{ meq./ml.} = 360 \text{ meq.}$$

$$\text{gm. } H_2SO_4 + \text{gm. } \text{Ø}SO_2Cl = 18.4 \text{ gm.}$$

$$\frac{\text{gm. } H_2SO_4}{0.0490} + \frac{\text{gm. } \text{Ø}SO_2Cl}{0.0883} = 360 \text{ meq.}$$

$$\frac{360\ (0.0490)(0.0883) - 18.4\ (0.0490)}{0.393} = H_2SO_4$$

H_2SO_4 16.7 gm.

Barium sulfate precipitation of water layer

0.5262 gm. of barium sulfate was obtained from a 1.0177 gm. aliquot of the water layer.

$$\text{gm. } BaSO_4 \times \frac{\text{eq. wt. } H_2SO_4}{\text{eq. wt. } BaSO_4} \times \frac{\text{wt. layer}}{\text{wt. aliquot}} = H_2SO_4$$

$$0.5262 \times \frac{98.08}{233.42} \times \frac{76.0}{1.0177} = H_2SO_4$$

H_2SO_4 16.5 gm.

<u>Sample Calculation</u> (continued)

Benzenesulfonyl chloride determination

water layer

H_2SO_4 + $\text{Ø}SO_2Cl$ = 18.4 gm.

16.7 gm. + $\text{Ø}SO_2Cl$ = 18.4 gm.

$\text{Ø}SO_2Cl$ 1.7 gm.

solvent layer

residue from distillation 3.1 gm.

total $\text{Ø}SO_2Cl$ 4.8 gm.

Reaction Data

The reactions were carried out in a 250 ml. separatory funnel equipped with a water cooled condenser. Agitation was achieved by bubbling a small stream of nitrogen through the reaction mass.

After the separation of the layers the acid was extracted with water which also caused some of the phenylsulfonyl benzene which was formed in the reaction to crystallize. The layers were then filtered to remove this solid.

The solvent was then stripped from the organic layer and the residue was refluxed for one hour with an excess of sodium hydroxide solution to convert the benzenesulfonyl chloride to the sodium salt of benzenesulfonic acid.

After cooling the mixture was filtered to remove the phenylsulfonyl benzene which had crystallized. Weighings at each step in the procedure allowed a determination of the amounts of products formed to be made.

Materials

The materials used in this work were:

Benzene

A.C.S. reagent grade special thiophene free
Catalog No. CB 209
Matheson Coleman and Bell

Benzenesulfonyl chloride

Fisher "reagent" grade
Catalog No. B 257
Fisher Scientific Company

Catalog No. 2862
Matheson Coleman and Bell

Carbon tetrachloride

Reagent grade
J.T. Baker Company

Chlorosulfonic acid

Practical grade
Catalog No. P 669
Distillation Products Industries Inc.

Material (continued)

Sulfuric acid

38 Normal 100.92 ± 0.15%

Hartmann - Leddon Company

These materials were used as received with no further purification.

TABLE I

Physical Properties

Compound	M. W.	M. P. °C	B. P. °C	Density gm./ml.	Solubility gm./100 gm. H$_2$O	Alc.	Eth.	Benz.
HCl	36.47	-111	-85		82.3^{0}	s.	s.	
$ClSO_3H$	116.52	-80	151.5	1.787	d.	d.		
H_2SO_4	98.08	10.49	340 d.	1.834	∞	d.		
CCl_4	153.84	-22.6	76.8	1.595	0.08^{20}	∞	∞	∞
C_6H_6	78.11	5.5	80.1	0.879	0.072^{22}	∞	∞	
øSO_2Cl	176.62	14.5	251.5	1.378	i.	v. s.	s.	
øSO_2NH_2	157.18	156			0.43^{16}	v. s. h.	v. s.	
øSO_2ø	218.26	125	377.81	1.252	sl. s. h.	s. h.	s.	s.
øSO_3H	158.17	50	d.		v. s.	v. s.	i.	sl. s.
øSO_3Na	180.16	450 d.			47	sl. s. h.		

Azeotropes

$HCl \cdot H_2O$	20.32 % HCl	108.6
$CCl_4 \cdot H_2O$	4.1 % H_2O	66
C6H6·H2O	8.83 % H_2O	69.25

EXPERIMENTAL RESULTS

TABLE II

Carbon Tetrachloride - Chlorosulfonic Acid - Sulfuric Acid Equilibrium Data

	Material	Weight gm.	Weight %
Run 1	CCl_4	12.445	24.4
	$ClSO_3H$	33.595	66.1
23°C	H_2SO_4	4.911	9.6
	End point overrun due to leaking burette		
Run 2	CCl_4	12.5	30.4
	$ClSO_3H$	27.7	67.4
23°C	H_2SO_4	0.9	2.2
Run 3	CCl_4	15.7	24.6
	$ClSO_3H$	44.9	70.4
23°C	H_2SO_4	3.2	5.0
Run 4	CCl_4	15.6	26.2
	$ClSO_3H$	41.9	70.3
23°C	H_2SO_4	2.1	3.5
Run 5	CCl_4	14.8	24.5
	$ClSO_3H$	42.6	70.6
23°C	H_2SO_4	3.0	5.1
Run 6	CCl_4	15.5	21.3
	$ClSO_3H$	51.8	71.2
24°C	H_2SO_4	5.5	7.5
Run 7	CCl_4	12.5	17.1
	$ClSO_3H$	51.6	70.4
25°C	H_2SO_4	9.2	12.6

	Material	Weight gm.	Weight %
Run 8	$ClSO_3H$	17.1	
	H_2SO_4	21.3	
25°C	CCl_4	-0.4	

98 % sulfuric acid was inadvertantly used. The water present reacted with the chlorosulfonic acid causing the loss in weight due to the evolution of gaseous hydrochloric acid.

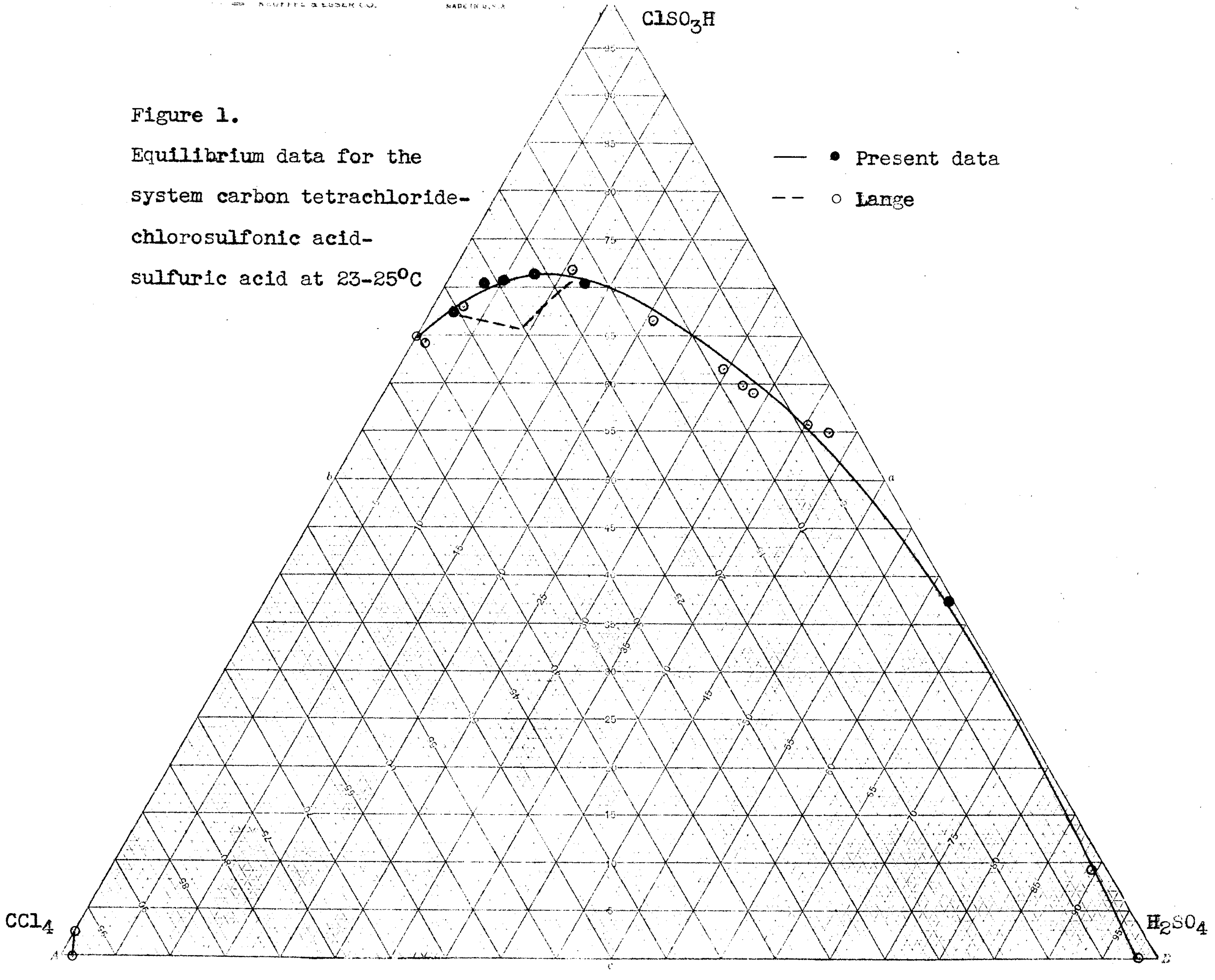


Figure 1.

Equilibrium data for the system carbon tetrachloride-chlorosulfonic acid-sulfuric acid at 23-25°C

TABLE III

Benzenesulfonyl Chloride - Carbon tetrachloride - Sulfuric Acid Equilibrium Data

	Material	Weight gm.	Weight %
Run 9	ØSO_2Cl	7.2	
23°C	CCl_4	175.9	

Two phases were not found when titrating benzenesulfonyl chloride with carbon tetrachloride.

	Material	Weight gm.	Weight %
Run 10	H_2SO_4	8.2	27.9
	ØSO_2Cl	16.6	56.5
23°C	CCl_4	4.6	15.6
Run 11	ØSO_2Cl	6.8	33.0
	H_2SO_4	12.5	60.7
23°C	CCl_4	1.3	6.3
Run 12	ØSO_2Cl	7.0	29.0
	CCl_4	17.0	70.6
23°C	H_2SO_4	<0.1	<0.4

Benzenesulfonyl chloride and carbon tetrachloride were miscible. Sulfuric acid when added formed a second phase immediately.

	Material	Weight gm.	Weight %
Run 13	ØSO_2Cl	13.2	59.2
	CCl_4	8.0	35.9
23°C	H_2SO_4	1.1	4.9

End point overrun slightly.

	Material	Weight gm.	Weight %
Run 14	H_2SO_4	7.8	20.7
	ØSO_2Cl	23.4	62.1
23°C	CCl_4	6.5	17.2

	Material	Weight gm.	Weight %
Run 15	H_2SO_4	25.8	73.5
	ØSO_2Cl	7.6	21.7
23°C	CCl_4	1.7	4.8
Run 16	H_2SO_4	16.3	48.4
	ØSO_2Cl	14.5	43.0
23°C	CCl_4	2.9	8.8
Run 17	H_2SO_4	36.9	89.3
	ØSO_2Cl	3.3	8.0
23°C	CCl_4	1.1	2.7
Run 18	H_2SO_4	11.4	37.5
	ØSO_2Cl	14.9	49.0
23°C	CCl_4	4.1	13.5
Run 19	H_2SO_4	8.7	19.4
	ØSO_2Cl	27.8	62.1
23°C	CCl_4	8.3	18.5
Run 20	ØSO_2Cl	15.9	64.4
	CCl_4	7.7	31.2
23°C	H_2SO_4	1.1	4.5
Run 21	H_2SO_4	4.8	12.4
	ØSO_2Cl	24.8	63.9
23°C	CCl_4	9.2	23.7
Run 22	ØSO_2Cl	13.4	45.9
	CCl_4	15.8	54.1
23°C	H_2SO_4	<0.05	<0.2

See note Run 12.

Run 23	ØSO_2Cl	4.9	19.9
	CCl_4	18.9	80.1
23°C	H_2SO_4	<0.05	<0.2

See note Run 12.

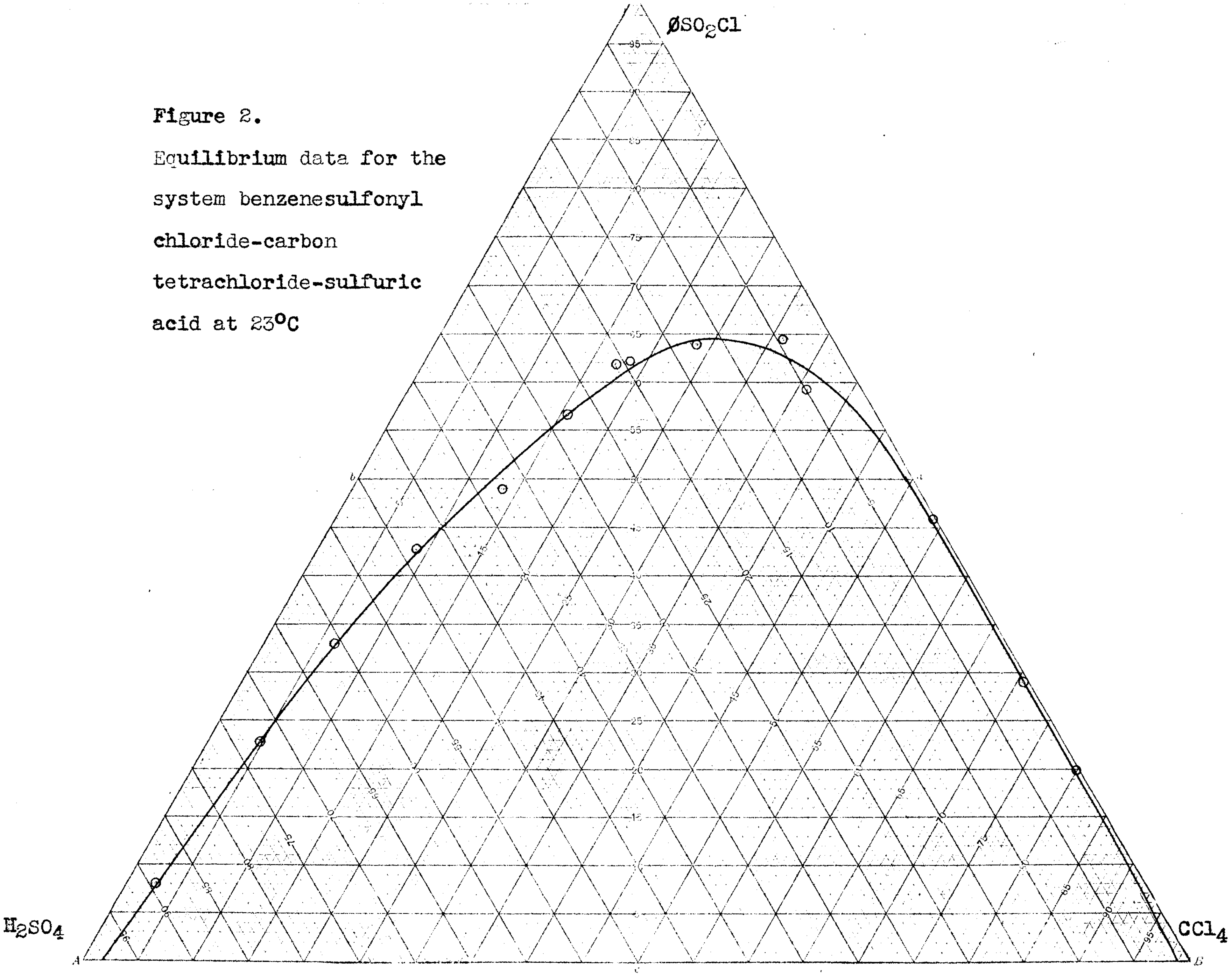


Figure 2.

Equilibrium data for the system benzenesulfonyl chloride-carbon tetrachloride-sulfuric acid at 23°C

TABLE IV

Benzenesulfonyl Chloride - Carbon Tetrachloride - Chlorosulfonic Acid - Sulfuric Acid Equilibrium Data

	Material	Weight gm.	Weight %
Run 27	ØSO_2Cl	8.6	18.9
	$ClSO_3H$	12.7	27.9
25°C	H_2SO_4	15.9	34.9
	CCl_4	8.4	18.4

Overran end point slightly.

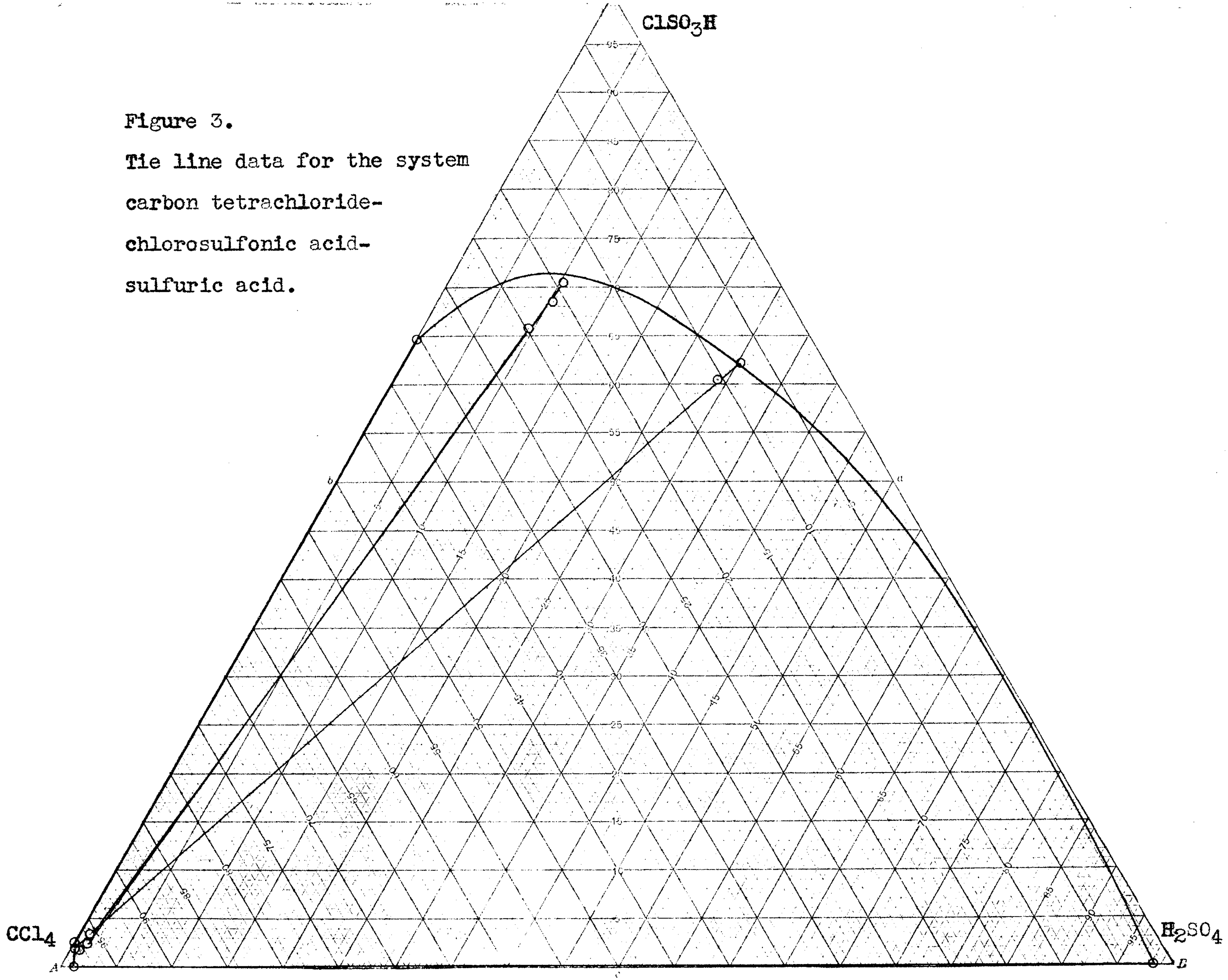
	Material	Weight gm.	Weight %
Run 28	ØSO_2Cl	7.2	17.3
	$ClSO_3H$	4.8	11.5
25°C	H_2SO_4	29.1	70.0
	CCl_4	0.5	1.2

TABLE V

Carbon Tetrachloride - Chlorosulfonic Acid - Sulfuric Acid Correlation of Tie Lines (9)

Run	a wt.fraction H_2SO_4 in acid layer	b wt.fraction CCl_4 in solvent layer	$\frac{1 - a}{a}$	$\frac{1 - b}{b}$
	Values from analysis of layers.			
9	0.1032	0.973	8.67	0.01747
10	0.0950	0.9648	8.60	0.0365
11	0.1025	0.977	8.75	0.0235
12	0.3018	0.9574	2.315	0.0445
13	0.2914	0.9788	2.09	0.02165
30	0.000	0.9749	∞	0.02575
31,38	0.9818	0.989	0.01855	0.01112
	Values obtained from analyzed values extrapolated to the equilibrium curve.			
9	10.5	97.96	8.52	0.02186
10	10.5	98.44	8.52	0.01585
12	29.5	97.83	2.05	0.0222
13	10.5	98.44	8.52	0.01585

Figure 3.
Tie line data for the system carbon tetrachloride-chlorosulfonic acid-sulfuric acid.



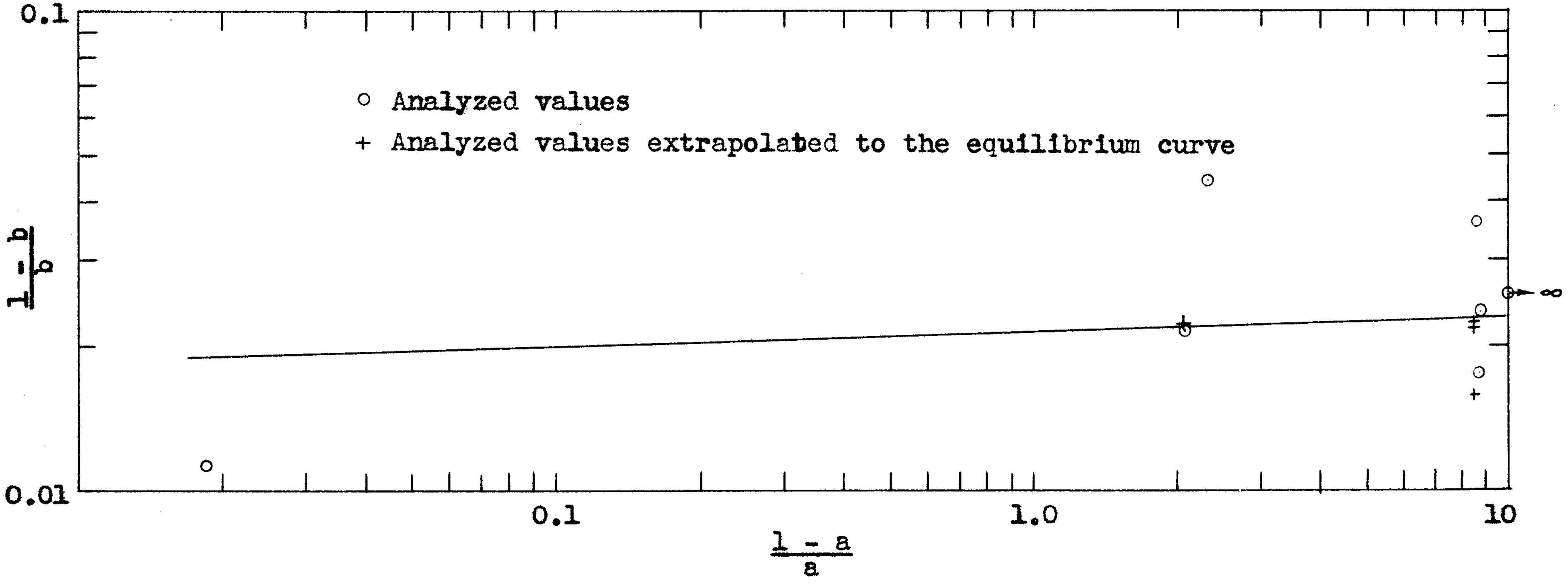


Figure 4. Correlation of tie lines in the system carbon tetrachloride- chlorosulfonic acid-sulfuric acid according to the method of Othmer and Tobias.

a wt. fraction H_2SO_4

b wt. fraction CCl_4

TABLE VI

Benzenesulfonyl Chloride - Carbon Tetrachloride - Sulfuric Acid Tie Line Data

	Material	Weight gm.	Weight %
Run 24	H_2SO_4	43.1	34.2
	$\text{Ø}SO_2Cl$	23.8	18.9
	CCl_4	59.2	46.9

The two layers formed were separated.

Solvent	65.5	53.3
Acid	57.3	46.6

An aliquot of the acid layer was drowned on crushed ice and neutralized with sodium hydroxide solution.

Sample	1.6408
NaOH	14.8 ml. of 1.8325 N.

The sample analyzed 78 % sulfuric acid, but the end point faded very rapidly. More sodium hydroxide was added. The sample now analyzed 82 % sulfuric acid, but the end point faded again.

Run 25 An attempt was made to form benzenesulfonamide from the sulfonyl chloride by reaction with ammonium hydroxide. The amide is a solid which is insoluble in water. On filtration of the precipitated product the filter broke through and the sample was lost.

Run 26 Run 25 was repeated. 10.5568 gm. of benzenesulfonyl chloride was reacted with 80 ml. of concentrated ammonium hydroxide solution. 7.9704 gm. of derivative were recovered. This recovery accounted for only 85 % of the benzenesulfonyl chloride. The filtrate on standing for several weeks had more crystals of the derivative form in it .

	Material	Weight gm.	Weight %
Run 29	CCl_4	7.0	21.7
	ϕSO_2Cl	16.7	58.1
	H_2SO_4	8.5	26.4

A two phase mixture was formed. The entire sample was drowned with 25 ml. of water. The water and solvent layers were separed. The water layer was neutralized with 206.5 ml. of 0.871 N. sodium hydroxide. The solvent layer was distilled.

	CCl_4	8.1	25.2
	ϕSO_2Cl	15.3	47.4
	H_2SO_4	8.8	27.3
Run 30	H_2SO_4	37.6	31.2
	ϕSO_2Cl	23.4	19.4
	CCl_4	59.4	49.3
	Acid layer	48.8	41.2
	Solvent layer	69.7	58.8

Acid layer analysis
A 13.3941 gm. aliquot of the 111.7 gm. water layer required 107.5 ml. of 0.878 N. sodium hydroxide for neutralization.

H_2SO_4	38.5	87.9
CCl_4	1.9	4.3
ϕSO_2Cl	3.4	7.8

Solvent layer analysis
The 47.5 gm. water layer required 20.0 ml. of 0.0953 N. and 44.2 ml. of 0.878 N. sodium hydroxide for neutralization.

H_2SO_4	2.0	2.9
CCl_4	56.6	81.7
ϕSO_2Cl	10.7	15.4

Run 31	H_2SO_4	24.0	21.9
	ϕSO_2Cl	47.2	43.0
	CCl_4	38.7	35.2
	Acid layer	32.7	30.3
	Solvent layer	75.2	69.8

Acid layer analysis

Water added	39.4
Solvent layer	7.1
Water layer	63.6

46.4 ml. of 0.878 N. sodium hydroxide neutralized a 5.8233 gm. aliquot.

	Material	Weight gm.	Weight %
Run 31 (continued)			
	H_2SO_4	18.8	60.1
	$\text{Ø}SO_2Cl$	10.5	33.5
	CCl_4	2.0	6.4

Solvent layer analysis

Water added	20.0
Solvent layer	70.9
Water layer	22.7

25.1 ml. of 0.878 N. sodium hydroxide neutralized a 6.6591 gm. aliquot.

H_2SO_4	2.9	3.9
$\text{Ø}SO_2Cl$	35.8	47.6
CCl_4	36.5	48.5

Run 32	H_2SO_4	19.9	19.8
	$\text{Ø}SO_2Cl$	39.8	39.7
	CCl_4	40.6	40.5
	Acid layer	23.0	23.4
	Solvent layer	75.1	76.6

Acid layer analysis

Water added	59.0
Solvent layer	4.6
Water layer	76.0

15.9 ml. of 0.878 N. sodium hydroxide neutralized a 2.9449 gm. aliquot.

0.5262 gm. of barium sulfate was obtained from a 1.0177 gm. aliquot.

H_2SO_4	16.5	71.8
$\text{Ø}SO_2Cl$	5.0	21.7
CCl_4	1.5	6.5

Solvent layer analysis

Water added	26.6
Solvent layer	74.1
Water layer	25.9

1.71 ml. of 0.878 N. sodium hydroxide neutralized a 6.0165 gm. aliquot.

0.2724 gm. of barium sulfate was obtained from an 11.0780 gm. aliquot.

H_2SO_4	0.26	0.4
$\text{Ø}SO_2Cl$	33.7	45.2
CCl_4	40.5	54.4

	Material	Weight gm.	Weight %
Run 33	H_2SO_4	21.6	21.6
	$\text{Ø}SO_2Cl$	32.2	32.4
	CCl_4	45.9	46.0
	Acid layer	25.6	26.5
	Solvent layer	71.0	73.5

Acid layer analysis

Water added	57.1
Solvent layer	2.8
Water layer	78.7

14.5 ml. of 0.878 N. sodium hydroxide neutralized a 2.3595 gm. aliquot.

The barium sulfate precipitate was lost when the crucible cracked.

H_2SO_4	19.5	79.8
$\text{Ø}SO_2Cl$	4.2	17.2
CCl_4	0.7	2.9

Solvent layer analysis

Water added	35.8
Solvent layer	67.9
Water layer	37.9

4.95 ml. of 0.878 N. sodium hydroxide neutralized a 4.5647 gm. aliquot.

0.8890 gm. of barium sulfate was obtained from a 11.7994 gm. aliquot.

H_2SO_4	1.2	1.7
$\text{Ø}SO_2Cl$	24.9	35.5
CCl_4	44.1	62.8

Run 34	H_2SO_4	34.6	30.9
	$\text{Ø}SO_2Cl$	5.3	4.7
	CCl_4	71.9	64.3
	Acid layer	36.4	33.7
	Solvent layer	71.5	66.3

Acid layer analysis

Water added	54.2
Solvent layer	2.0
Water layer	87.2

23.2 ml. of 0.878 N. sodium hydroxide neutralized a 2.6038 gm. aliquot.

The separation of the water extraction was poor, the solvent layer was emulsified.

	Material	Weight gm.	Weight %
Run 34 (continued)			
	Solvent layer analysis		
	Water added	40.9	
	Solvent layer	69.6	
	Water layer	40.7	
	12.45 ml. of 0.878 N. sodium hydroxide neutralized the water layer.		
	H_2SO_4	00.536	0.75
	ϕSO_2Cl	3.6	5.0
	CCl_4	67.4	94.2
Run 35	H_2SO_4	28.2	26.2
	ϕSO_2Cl	56.9	52.8
	CCl_4	22.6	21.0
	Acid layer	40.4	38.0
	Solvent layer	66.0	62.0
	Acid layer analysis		
	Water added	103.7	
	Solvent layer	12.3	
	Water layer	131.2	
	5.12 ml. of 0.878 N. sodium hydroxide neutralized a 1.1647 gm. aliquot.		
	H_2SO_4	21.2	52.9
	ϕSO_2Cl	16.8	41.9
	CCl_4	2.1	5.2
	Solvent layer analysis		
	Water added	66.3	
	Solvent layer	57.5	
	Water layer	73.1	
	20.2 ml. of 0.878 N. sodium hydroxide neutralized a 9.1228 gm. aliquot.		
	H_2SO_4	6.2	9.5
	ϕSO_2Cl	40.0	61.5
	CCl_4	18.9	29.6

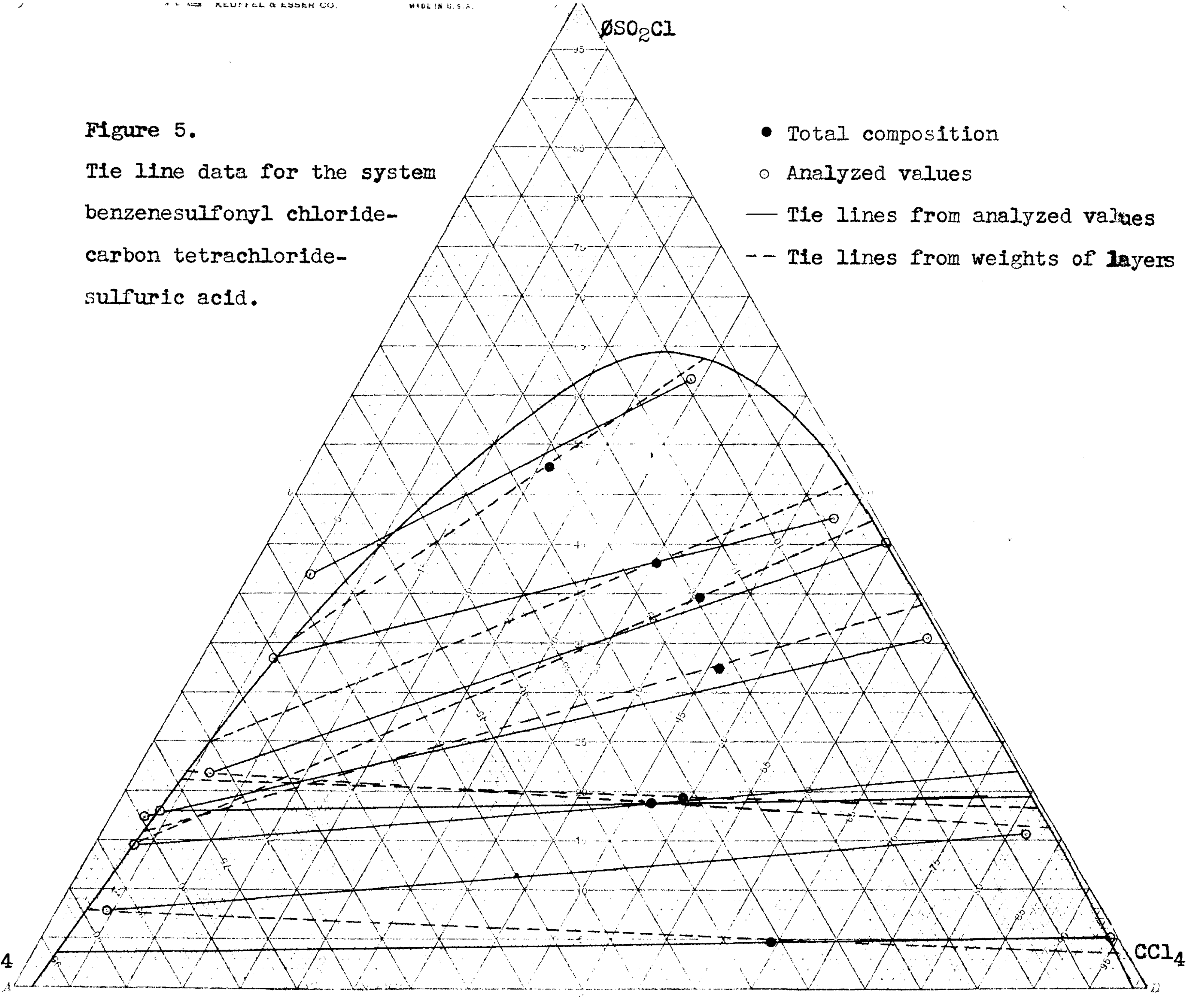


Figure 5. Tie line data for the system benzenesulfonyl chloride-carbon tetrachloride-sulfuric acid.

TABLE VII

Benzenesulfonyl Chloride - Carbon Tetrachloride - Sulfuric Acid Correlation of Tie Lines

Run	a wt. fraction H_2SO_4 in acid layer	b wt. fraction CCl_4 in solvent layer	$\frac{1-a}{a}$	$\frac{1-b}{b}$
	values from weights of layers			
24	0.735	0.832	0.361	0.202
30	0.745	0.813	0.342	0.230
31	0.700	0.480	0.428	0.924
32	0.823	0.518	0.215	0.930
33	0.805	0.608	0.242	0.645
34	0.893	0.955	0.120	0.047
35	0.575	0.291	0.739	2.44
	values from analysis of layers			
24	0.780	0.797	0.282	0.255
24	0.820	0.775	0.219	0.291
30	0.860	0.817	0.163	0.226
31	0.601	0.485	0.664	1.06
32	0.718	0.544	0.393	0.838
33	0.798	0.628	0.253	0.593
34	0.947	0.942	0.056	0.062
35	0.529	0.290	0.891	2.45
	values from analyzed values extrapolated to the equilibrium curve			
30	0.903	0.833	0.1075	0.200
31	0.600	0.498	0.666	1.008
32	0.695	0.543	0.439	0.841
33	0.785	0.637	0.274	0.585
34	0.944	0.940	0.0593	0.0639
35	0.420	0.308	1.38	2.25

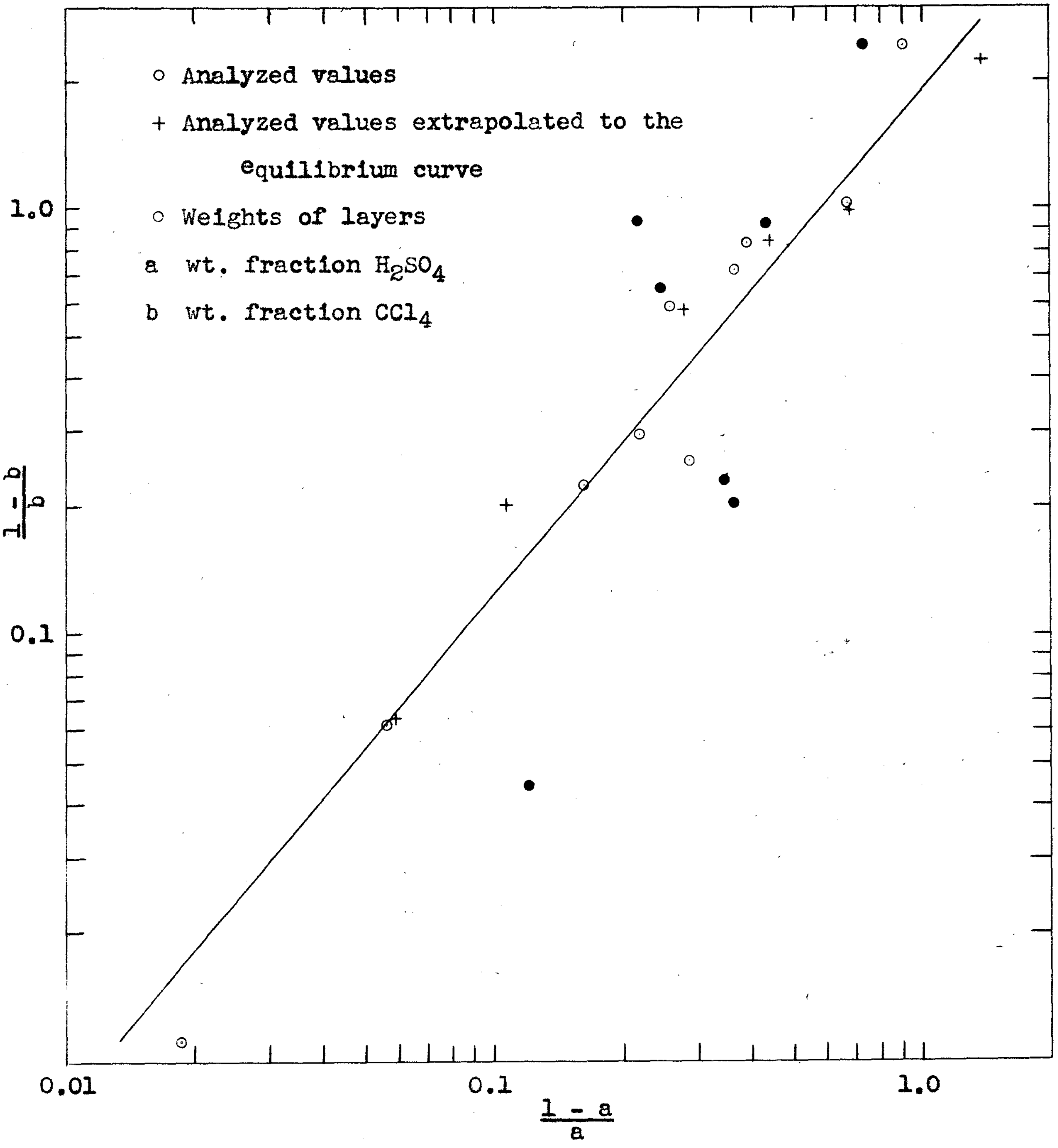


Figure 6. Correlation of the tie lines in the system benzenesulfonyl chloride-carbon tetrachloride-sulfuric acid according to the method of Othmer and Tobias.

TABLE VIII

Reaction Data

Run 36 Reaction charge

$ClSO_3H$	61.5 gm.
CCl_4	76.3
C_6H_6	23.9

During the reaction there were losses of liquid from the top of the condenser.

Acid layer	61.5
Solvent layer	80.6

Acid layer analysis

Water added	92.0
Solvent layer	4.7
CCl_4	1.0
$ØSO_2Ø$	1.1
$ØSO_2Cl$	2.6

The water layer of the water extraction of the acid layer was extracted with benzene which after separation was evaporated. 0.4 gm. $ØSO_2Ø$ was recovered.

Solvent layer analysis

Water added	67.3
Solvent layer	58.2
CCl_4	43.2
$ØSO_2Ø$	2.0
$ØSO_2Cl$	13.0

Nothing was recovered from the benzene extraction of the water layer.

2.6 gm. $ØSO_2Ø$ was recovered from the filtration after reaction.

Total recoveries

$ØSO_2Ø$	5.7
$ØSO_2Cl$	15.6

Run 36 (continued)

Yield

$\text{Ø}SO_2\text{Ø}$	$\frac{78.11}{23.9} \times 2 \times \frac{3.1}{218.26}$	= 9.3 %
$\text{Ø}SO_2Cl$	$\frac{15.6}{176.62} \times \frac{78.11}{23.9}$	= 28.9 %

Run 37 Reaction charge

$ClSO_3H$	73.2 gm.
CCl_4	72.4
$NaCl$	15.0
C_6H_6	25.9

There were liquid losses from the top of the condenser during the reaction. The reaction mass on standing, after the agitation had been stopped, set up in a porous solid form. Water was added until the solid mass was disolved. The organic layer was separated and the water layer was extracted with benzene.

Solvent layer analysis

Solvent layer	53.4
CCl_4	39.0
$\text{Ø}SO_2\text{Ø}$	3.4
$\text{Ø}SO_2Cl$	15.3

Water layer analysis

After evaporation of the benzene from the extraction 0.5 gm. $\text{Ø}SO_2\text{Ø}$ was recovered.

Total recoveries

$\text{Ø}SO_2\text{Ø}$	3.9
$\text{Ø}SO_2Cl$	11.9

Yield

$\text{Ø}SO_2\text{Ø}$	$\frac{78.11}{25.9} \times 2 \times \frac{3.9}{218.26}$	= 10.8 %
$\text{Ø}SO_2Cl$	$\frac{78.11}{25.9} \times \frac{11.9}{176.62}$	= 20.4 %

DISCUSSION

Methods

In general, of the methods employed to obtain the data given, the cloud point determinations for the equilibrium curves were found to be the most reliable. Several times almost exact duplicates of compositions were found while doing this work. Runs 3 and 5 in Table II and Runs 14 and 19 in Table III illustrate this. These duplications were not made intentionally but were found in the course of making determinations at random intervals of composition along the curve.

The chemically analyzed samples showed less reliability. This is due in part to the number of transfers involved in making up the samples, separating the layers, extracting the layers with water, and reseparating the water extraction layers. There were measurable losses in each one of these operations. The most noticeable was a particularly large loss in the acid layer of the original two phase samples. On transfering the sample to the separatory funnel the glass of the flask used in making up the sample was wetted by the acid layer and several rinses with the organic material of the sample would not completely remove the acid material from the flask. The other transfers did not show this characteristic.

It was found early in this work that the acid determination method described in Lange's work was not reliable in the presence of benzenesulfonyl chloride. The phenolphthalein end point that was obtained by this method faded very rapidly and the concentration of acid found was dependent upon how rapidly the titration was carried out. Therefore a new method of determining the compositions was developed. At first it was assumed that the benzenesulfonyl chloride remained in the solvent layer of the water extraction but it was found that the material balances on this material were poor, (Runs 24 & 30). Once it was realized that the benzenesulfonyl chloride was being distributed between the acid and solvent layers in the water extraction and this situation was corrected for, the material balances became more reliable,(Runs 31-35).

Another source of error in the analytical results obtained in this work was the fact that some of the separations were made before the layers in the separatory funnel had completely cleared of very fine droplets of material from the other layer. At times it was necessary for the samples to stand for several days before the layers were clear.

Equilibrium Data

Carbon tetrachloride - Chlorosulfonic acid - Sulfuric acid

In the earlier work on this system (5) the data which was presented gave an equilibrium saturation curve of an odd configuration. The initial work in this paper was done to check this. Table I Runs 1 through 8 present new data on this system. Figure 1 shows the curve derived from the equilibrium data obtained in this paper and the previous work. Figure 1 does not include data obtained by analysis of extraction layers, only that obtained by phase equilibrium methods which seem to be more reliable.

The point which was plotted for Run 8 was calculated assuming that the water present in the system hydrolyzed the chlorosulfonic acid to form sulfuric acid and hydrochloric acid. The loss in weight in the sample between the addition of the sulfuric acid and the weighing after the addition of the carbon tetrachloride was assumed to be due to the loss of hydrochloric acid, which left the system as a gas. This method gives a point which lies close to the curve obtained by Lange and on the curve obtained in this work.

The new data which was obtained presents a different shape for the equilibrium curve which does not have the odd configuration found in the previous work. It appears that the data which had been obtained by the analysis of equilibrium layers was responsible for this difference in the shapes of the curves. This error in the analysis could be due to a poor separation of the layers due to the material in the bottom layer wetting the glass and not draining properly.

Benzenesulfonyl chloride - Carbon tetrachloride - Sulfuric acid

The equilibrium curve obtained from the data had only one immiscible binary as would be predicted from Lange's work if sulfuric acid containing no water were used. The miscibility of the benzenesulfonyl chloride - sulfuric acid pair was complete over all of the range tested. The immiscibility found in Lange's work was due to the fact that the sulfuric acid used contained some water which would be immiscible with the benzenesulfonyl chloride. The sulfuric acid used in this work contained no free water therefore the pair was found to be completely miscible.

The equilibrium curve determined by the data is smooth and no difficulties were experienced in obtaining this data.

Benzenesulfonyl chloride - Chlorosulfonic acid - Sulfuric acid

From the data obtained in this work showing the miscibility of benzenesulfonyl chloride and sulfuric acid plus that obtained by Lange this system would appear to be completely miscible.

Benzenesulfonyl chloride - Carbon tetrachloride - Chlorosulfonic acid - Sulfuric acid

The data that has been obtained in this system does not appear to be very accurate. In the present work the chlorosulfonic acid used in Runs 27 and 28 had been stored for approximately nine months and upon reuse it was found that the cap on the bottle, a phenolic resin, had decomposed to the point where it was not sealing the bottle properly. Therefore the sulfuric acid concentration is probably higher than that reported. On plotting these points on a three dimensional model of the tetrahedron representing the quaternary system it was found that the points were not close to the expected equilibrium surface.

The data obtained by Lange for this system suffers from the fact that it was obtained by analytical methods which were found to be inaccurate and develops an oddly shaped equilibrium surface.

Tie Lines

Carbon tetrachloride - Chlorosulfonic acid - Sulfuric acid

Lange's data was used to correlate the tie lines in this system. The correlation method used is that described by Alders (1) page 59 which was developed by Othmer and Tobias. In order to obtain a more exact correlation than that from the data available more extensive work would be necessary in the area of the ternary system approaching one hundred percent carbon tetrachloride. This work does not seem to be warranted since the area of solubility is small enough to assume that all of the tie lines in this system will pass through the one hundred percent carbon tetrachloride point if extrapolated through the soluble area of the graph. Since one point on the correlation plot is at infinity it would appear that the line for this plot is nearly horizontal.

Benzenesulfonyl chloride - Carbon tetrachloride - Sulfuric acid

The tie lines determined in this system were obtained by two different methods. The weights of the equilibrium layers and the composition of the original sample were used to determine one set of lines. The analysis of the equilibrium layers was used to find the other. A third set of points used in the correlation was determined by extrapolating the tie lines determined by analysis to the equilibrium curve, This was done because most of the analyzed compositions did not fall on the equilibrium curve.

The tie line determined from the weights of the layers were subject to a wide variation in equilibrium composition with a small change in the weight of either of the layers. These lines were valuable for showing a trend in the change in equilibrium compositions but could not be relied upon for any exact measurements.

More consistent results were obtained from the tie lines determined by analysis. These results while not exact gave a correlation by the method used.

The method used for correlating the tie lines has the defect of requiring much greater accuracy in the determination of points near the one hundred percent area of either of the two immiscible components. Also if there are two immiscible pairs in the system there will be one point at infinity. Both of these points are apparent in the system carbon tetrachloride - chlorosulfonic acid - sulfuric acid.

Several attempts were made to correlate the data for the ternaries involved in this work to give an indication of the properties of the quaternary system, (2,5,8 & 12). None of these attempts was very successful due to the limited amount of data available on the quaternary and the inaccuracy of the data.

The original methods tried were those of Hunter (8) and Smith (12) but the work of Francis (5) showed that these methods were valid only if there was one immiscible pair and if the equilibrium curves were nearly parallel to the sides of the triangular diagrams. Since the system investigated has two immiscible pairs it would appear that more extensive data is necessary before the equilibrium curve can be determined.

Reaction Data

Two reactions were carried out to determine the effect of the presence of the solvent and the presence of salt on the reaction when stoichiometric amounts of the reactants were used.

In both of the reactions the material balances were poor. This was due in part to a small eruption in each reaction which carried liquid through the condenser and a fine spray of liquid which issued from the top of the condenser during the reaction even when the nitrogen sparging was stopped.

The reactions were carried out in a separatory funnel to obtain data on reaction rates by separating the acid and solvent layers of the reaction after a specified time. This did not prove feasible because in Run 36 the layers did not separate readily after the agitation was stopped and Run 37 set up into a solid mass on standing.

There was no cooling on the reaction except that supplied by the condenser. The temperatures therefore approached the reflux temperature of the solvent which is above the 20-25°C given in the literature.

In future reactions it was planned to carry out the work in a suitable reaction kettle or flask which would be cooled by a water and ice bath. The reaction would be stopped when obtaining rate data by drowning the reaction mass with water at the proper time. It was also planned to determine the amount of benzenesulfonic acid formed by neutralizing the acid layer with ammonia to precipitate benzenesulfonamide.

In both reactions there was a large percentage of benzene which was unaccounted for by losses if it were assumed that the benzene losses were of the same order of magnitude as those of carbon tetrachloride. It is possible that this benzene can be accounted for by the formation of benzenesulfonic acid which has a high water solubility and would not be recovered in the benzene extraction of the water layer.

There were indications of a small amount of unreacted benzene during the solvent stripping. During previous strippings the head temperature of the still dropped several degrees at the end of the carbon tetrachloride cut but in Runs 36 & 37 there was a slight rise in the temperature before it dropped at the end of the carbon tetrachloride cut.

No definite conclusions about the reaction can be made at the present time. It appears that when stoichiometric amounts of the reactants are combined at high temperatures, above 50°C, large amounts of by products are formed.

CONCLUSIONS AND RECOMMENDATIONS

The ternary system carbon tetrachloride - chlorosulfonic acid - sulfuric acid is composed of two single phase regions separated by a two phase region which is bounded by smooth curves.

The ternary system benzenesulfonyl chloride - chlorosulfonic acid - sulfuric acid is completely miscible.

The ternary system benzenesulfonyl chloride - carbon tetrachloride - sulfuric acid contains one immiscible pair and its two phase region is bounded by a smooth curve.

The quaternary system under investigation will be useful in the chlorosulfonation of benzene only if all of the benzene is consumed in the reaction. If all of the chlorosulfonic acid is consumed leaving excess benzene in the system it would become necessary to investigate the quaternary benzene - benzenesulfonyl chloride - carbon tetrachloride - sulfuric acid. This at the present time does not appear to be necessary due to the fact that in present batch operations an excess of chlorosulfonic acid is necessary to attain the desired product in reasonable yields.

If it is found that the addition of salt to the reaction to remove the sulfuric acid as it is formed is advantageous in increasing yields it will become necessary to investigate the systems which would result if sulfuric acid were replaced by sodium acid sulfate.

Much more work is required on the reaction to determine rates, and the ratios of reactants required to obtain optimum yields and recoveries. This information will also be helpful in designing the reaction equipment.

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