THE SEPARATION OF ETHYLBENZENE
AND m-XYLENE

By

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INTRODUCTION

For over seventy-five years, beginning with the chemistry of coal tar, chemists have tried to devise an effective commercial method of separating the xylene isomers and ethylbenzene from each other. The mixture occurs in the so-called light-oil fraction obtained in destructive distillation of coal. Also large quantities of the mixture have been made available in recent years by the hydroforming process used in the petroleum industry for manufacturing high-octane gasolines from poor-grade stock containing mostly paraffins. This process reforms many of the paraffins to aromatic hydrocarbons, which greatly increase the octane rating of the fuel. At present the mixture can either be added to the fuel or sold as a solvent; in either case a much lower price is obtained than could be gotten if the components were sold separately. o-Xylene can be separated fairly easily at present by fractional distillation, and p-xylene rather less readily by fractional crystallization (109a). Each of the components is valuable in the resin, plastics, or synthetic fiber industry, and their uses need not be discussed further here. Many methods have been investigated for this separation, and most of these will be discussed in the historical part of this thesis.

The two methods tested in this study, extractive distillation and complex formation, were selected after consideration of three factors:

(1) time available for the work, (2) ease of experimental study, and (3) promise, as judged from the literature. The theory and results of these two methods will be described separately.

HISTORICAL

An Outline of Possibilities for the Commercial Separation of Ethylbenzene and m-Xylene

I. Recovery of Components as Such

A. Physical Methods

1. Fractional distillation. Comprehensive data on physical properties of ethylbenzene and m-xylene are given by Willingham (125). No vapor pressure data are available for the xylenes and ethylbenzene at superatmospheric pressures. However, a plot of 1/T versus $\log_{10}P$ for m-xylene and ethylbenzene does not indicate appreciable difference in boiling points at pressures directly above atmospheric (49). The boiling-point difference between m-xylene and ethylbenzene becomes approximately 21° at 5 mm. pressure (Figure 1), but a fractionating column and refrigerated condenser of tremendous capacity would be necessary to make such a process feasible. Considerable differences in the boiling points of m-xylene and p-xylene are also noted at reduced pressures. Separation of the mixture ethylbenzene-m-xylene-p-xylene by fractional distillation at atmospheric pressure would require such elaborate equipment as to be out of the question commercially (109).

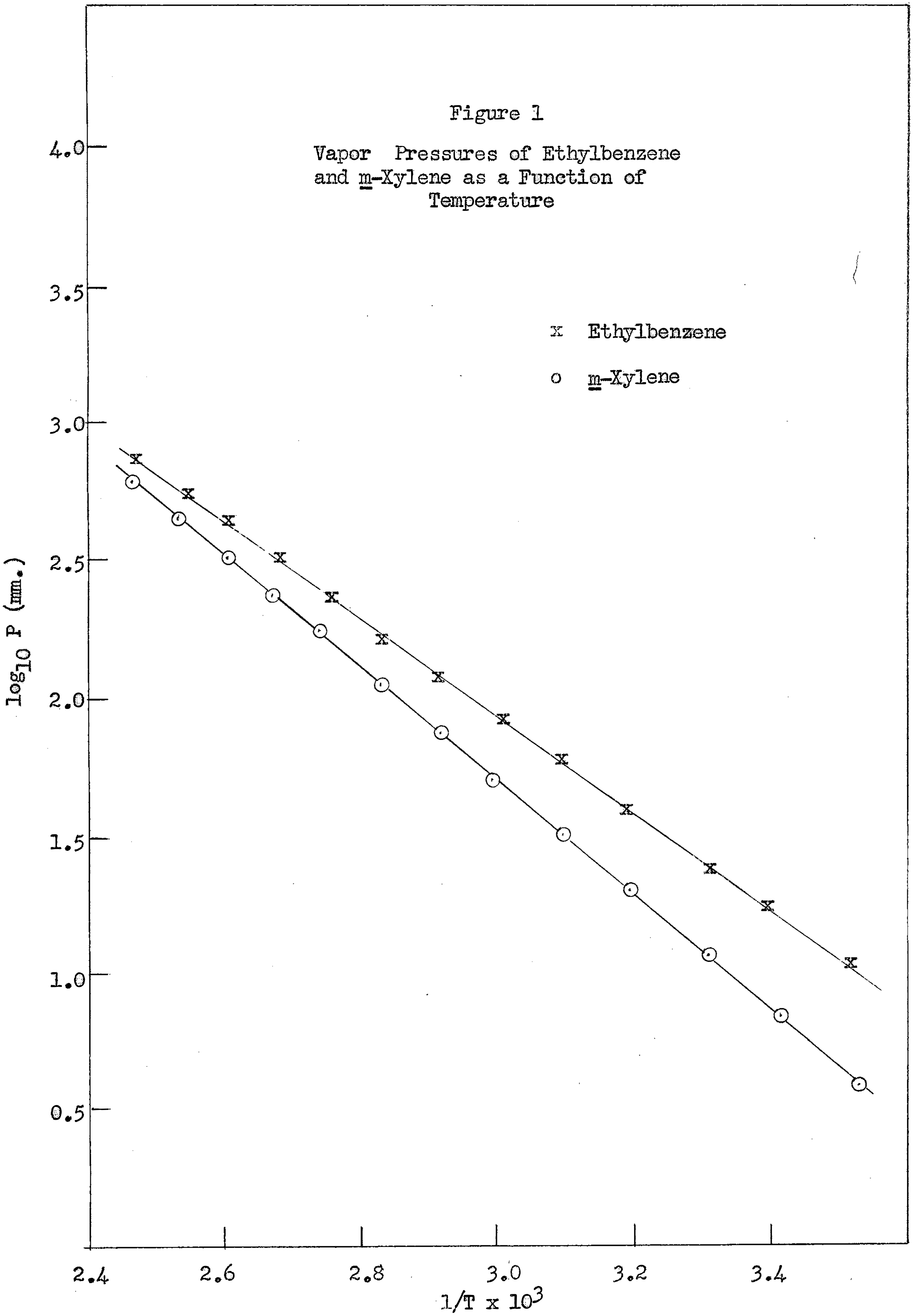


Figure 1

Vapor Pressures of Ethylbenzene and m-Xylene as a Function of Temperature

2. Selective azeotropic distillation. The general principles of this method of separation are discussed by Mair, Glasgow, and Rossini (73). Several azeotropes are reported for one of the compounds and not the other. However, other considerations such as breaking of the resulting azeotrope, stability of the azeotroping agent, and cost of the agent must be considered in such a process (33). Known azeotropes which might possibly be used in such a separation are listed in Table I (46). Many more examples of azeotrope formation can be found in the literature (46, 61, 62); the book by Horsley (47) is the most complete compilation. Several disagreements between workers as to whether azeotropes form with certain compounds are noted (46).

3. Selective extractive distillation. General discussions of the theory and technique of extractive distillation are given by White (124), Colburn and Schoenborn (17), and Stage (112). Benedict and Rubin (10) compare extractive and azeotropic distillation. Several references give relatively simple laboratory apparatuses for determining a suitable solvent for extractive distillation (16, 35, 110, 111). Chu *et al.* (19) investigated various extractants for separation of *m*- and *p*-xylenes with negative results. Two patents (88, 91) have been issued for the separation of xylenes and ethylbenzene by extractive distillation with antimony halides, although Sherwood (109) indicates this is a poor method for the separation.

Table 1

Selected Azeotropes of Ethylbenzene and the Xylenes

Agent (A)	Hydrocarbon (B)	Azeotrope b. p., °C	Azeotrope Composition, % A
1,2-Dibromoethane	ethylbenzene	131.1	90
	m-xylene	non-azeotrope	—
Methyl chloroacetate	ethylbenzene	131.3	97
	m-xylene	127.2	62.5
2-Methoxyethanol	ethylbenzene	116.5	54
	xylenes	min. b.p. azeotropes	—
Isobutyl alcohol	ethylbenzene	107	80
	m-xylene	107	87
	p-xylene	107	83
	o-xylene	non-azeotrope	—
2-Furaldehyde	ethylbenzene	non-azeotrope	—
	xylenes	138-40	5-13
Diethyl carbonate	ethylbenzene	124	77
	m-xylene	non-azeotrope	—
Paraldehyde	ethylbenzene	non-azeotrope	—
	p-xylene	non-azeotrope	—
	m-xylene	134	30
n-Hexyl alcohol	ethylbenzene	non-azeotrope	—
	m-xylene	136	50
	o- and p-xylene	non-azeotrope	—

Separation by ordinary fractional distillation is enhanced by using boron trichloride as an additive to the mixture before distillation (63). Many possibilities exist, ranging from the case where the extracting liquid simply selectively dissolves one component to the case where a complex is formed with one component (9, 10, 17, 54, 111, 112). Even extractive distillation with a hydrotropic solution has been studied for the separation of xylenes, with some success (66). In the past most work has been done on the separation of paraffins from aromatic substances, hereafter referred to simply as aromatics (28, 54, 110), and paraffins from cycloparaffins (24). Due to the fact that the method had apparently been little studied in connection with this separation, its ease of experimental study, and its obvious ease of application to commercial processes, study along this line was undertaken.

4. Selective liquid-liquid extraction.
    a. Simple extractants. This method has apparently not been used in the present case extensively owing to the similar solubilities of the compounds (34, 38, 40). m- and p-Cresols have been separated by fractional extraction on a laboratory scale (20) and aromatics have been separated from aliphatics with ethylenediamine (22). In a slightly different case two immiscible liquids serve to separate the mixture,

n-pentane and sulfur dioxide being the common pair used (67, 113). The method would be easy to study experimentally provided a suitable analytical method were available.

b. Hydrotropic effect. The theory of this phenomenon is given by Lindau (65). Much isolated information is available on the solubilities of various organic compounds in these salt solutions (12, 13, 29, 37, 43, 64, 84, 85, 120, 121). There seems to be no relationship between the natures of the solute and the substance solubilized (74). Some work has been done in separating aromatics by this method; thus aniline and dimethylaniline can be separated effectively (68), and lithium iodide can be used satisfactorily in separating aniline and benzyl alcohol. Most work has been done with hydrocarbons containing nitrogenous and oxygenated substituents (121). Better results are obtained where compounds differ appreciably in structure, for example, aromatics and aliphatics (84). There is little theory to go by; most common hydrotropic materials such as salts of xylenesulfonic acid have been tried but apparently none with the direct object of separating xylenes and ethylbenzene. Experimental work would be rather easy and the method could be adapted commercially; however, the chances of finding the proper combination of materials for extraction, if there is one, would be uncertain.

5. Selective adsorption. Much work has been done in separating aromatic and paraffinic hydrocarbons by this method (41, 83). One process is the basis for an industrial separation of aromatics from mixed hydrocarbon streams (83). This process, which involves adsorption on silica gel, does not suggest much selectivity between aromatics (114). Various aromatics, including the xylenes and ethylbenzene, have been separated with some success on a laboratory scale by this method; however, in no case has a pure isomer been obtained by one pass over an adsorbent (41, 69, 83, 86, 95). Mair, Gaboriault, and Rossini (69) obtained a 90% yield of p-xylene by passing a 50-50 mixture of o- and p-xylenes over silica gel. Comprehensive studies of adsorption of hydrocarbons on other materials have been made (45, 115). However, the three xylenes and ethylbenzene differ very little in their adsorbability from acetone on active carbon (121a). m-Xylene should be more adsorbed on silica gel than ethylbenzene (115). Adsorption of these compounds has been related to temperature by Spengler and Krenkler (115) and to molecular size and structure by Mair, Gaboriault, and Rossini (69). It appears that some separation can be obtained by adsorption methods but the feasibility of the method is doubtful; in particular, desorption without deactivating the adsorbent is difficult.

6. Thermal diffusion

   a. Gaseous thermal diffusion depends primarily on molecular volume differences. All components considered here have identical molecular weights and very similar densities, so the method was not considered in this work. Sunier and Rosenblum describe the theory of gas separation by this method (107).

   b. Liquid thermal diffusion, a relatively new technique, has been investigated for separation of various two- and three-component systems by Jones and Milberger (50). The separation of ethylbenzene and m-xylene was not considered, but since these authors indicate that separations depend primarily on differences in molecular configuration, the method is possible. Only small-volume apparatuses have been used so far and no information has been published on any commercial use of the method.

7. Fractional crystallization (11, 70, 87). Although considerable differences exist in the freezing points of these compounds, it is feasible to separate only p-xylene by this method (11). This is presently being carried out commercially (23, 109a). The extremely low temperatures required in other cases would be prohibitively expensive.

8. Other conceivable physical methods, such as fractional flotation in a foam and fractional entrapment in a gel

structure, have not been mentioned in the literature.

B. Chemical Methods

1. Clathrate complex formation (96, 97, 99). Apparently no work has been done on separation of isomeric aromatic hydrocarbons by this method, but theoretically it is sound. The difference in molecular size and shape of m-xylene and ethylbenzene should be great enough to permit a separation since complex formation depends on these molecular dimensions (96, 97, 98, 99). Nickel cyanide complexes have been used to trap benzene from solutions of aliphatics (32, 100). Phenol, thiophene, and aniline also form nickel cyanide complexes, but none of the other simple derivatives of benzene do (100). Urea forms such complexes with n-paraffins and thiourea with isoparaffins (101, 102, 116). This can be used as the basis for separation of such compounds. Prediction of complex formation is hindered by the fact that it is possible for the vacant places in crystal structure to change shape on complex formation (97). A complexing compound with strong crystal forces (hydrogen bonding) would be the best one to try. Other factors to consider would be solubility and crystallizing properties of the complexing agent. An enormous amount of work would be required to survey enough compounds to obtain success in this separation, if indeed that could be done. Most of the substances known to form clathrate complexes

with aromatic hydrocarbons are complex and expensive organic molecules.

2. Selective formation of a Lewis acid-Lewis base complex. Compounds such as $AlCl_3$, HF, BF_3, and SbX_3 will serve as the acid, and the hydrocarbon as the base. This has been much studied in the petroleum industry for aromatic-paraffin mixtures and also, though much less, for aromatic mixtures (81). McCaulay (81) reports that m-xylene of 95% purity can be obtained from mixtures of other xylenes and that all xylenes can be separated from ethylbenzene by extraction with $HF-BF_3$. Some migration of the ethyl group occurs owing to the influence of the $HF-BF_3$, amounting to 14% of the charge in one case. The xylenes react with $AlCl_3$ to give a heavy red oil of composition $(CH_3)_2C_6H_4 \cdot AlCl_3$ (25). Relative basicities of various aromatic hydrocarbons have been determined, by various methods, by McCaulay (82) and Andrews (1). Relatively stable solid complexes of aromatics and $SbCl_3$, including the xylenes and ethylbenzene, have been studied cryoscopically (105), by viscosity methods (56, 57), and by phase rule methods (75-79). $ArH \cdot SbCl_3$ and $ArH \cdot 2\ SbCl_3$ type complexes both exist, the latter ratio at room temperature. No compounds were found with cyclohexane and cyclohexene (78). $SbBr_3$ forms similar complexes. The properties of some of these complexes, obtained by phase rule studies, are listed in Table II. Aromatic compound complexes with halogens (55,

Table II

Properties of Adducts of Antimony Trihalides and Simple Arenes

Composition*	M. P. of Complex, °C.	Transition Point, °C.	Transition or Comment	Reference
$2\ SbCl_3 \cdot B$	79	--	No other compounds found	68
$SbCl_3 \cdot T$	15-16	11	$SbCl_3 \cdot T \rightleftarrows 2SbCl_3 \cdot T$	70
$2SbCl_3 \cdot T$	42.5	--	--	70
$SbCl_3 \cdot E$	39	35	$SbCl_3 \cdot E \rightleftarrows 2SbCl_3 \cdot E$	70
$2SbCl_3 \cdot E$	37	37	$2SbCl_3 \cdot E \rightleftarrows 2SbCl_3 + E$	70
$SbCl_3 \cdot M$	7-8	-2	$SbCl_3 \cdot M \rightleftarrows 2SbCl_3 \cdot M$	69
$2SbCl_3 \cdot M$	38	--	--	69
$SbCl_3 \cdot O$	19	19.5	$SbCl_3 \cdot O \rightleftarrows 2SbCl_3 \cdot O$	69
$2SbCl_3 \cdot O$	33.8	--	--	69
$SbCl_3 \cdot P$	56	55	$SbCl_3 \cdot P \rightleftarrows 2SbCl_3 \cdot P$	69
$2SbCl_3 \cdot P$	70	58	$2SbCl_3 \cdot P \rightleftarrows 2SbCl_3 \cdot P$	69
$2SbBr_3 \cdot B$	92.5	--	No other compounds found	68
$SbBr_3 \cdot T$	9	-1	$SbBr_3 \cdot T \rightleftarrows 2SbBr_3 \cdot T$	70
$2SbBr_3 \cdot T$	39	30	$2SbBr_3 \cdot T \rightleftarrows 2SbBr_3 + T$	70
$SbBr_3 \cdot E$	33	29	$SbBr_3 \cdot E \rightleftarrows SbBr_3 + E$	70
$SbBr_3 \cdot M$	13.5	12.5	$SbBr_3 \cdot M \rightleftarrows 2SbBr_3 \cdot M$	69
$SbBr_3 \cdot O$	24	--	No mention of other compounds	69
$SbBr_3 \cdot P$	67.5	--	No other compounds were found	69

* B = benzene, T = toluene, E = ethylbenzene, M = *m*-xylene, O = *o*-xylene, P = *p*-xylene.

56) and with silver ions (1, 2, 3) in aqueous solution have been studies by Andrew and Keefer. The success of the HF-BF_3 extraction work suggested work with other acidic compounds, and the complexes of aromatics with $SbCl_3$ have now been studied by a vapor pressure method.

3. Selective sulfonation of m-xylene. m-Xylene can be selectively sulfonated in the presence of other xylenes and ethylbenzene (36, 117). Also selective hydrolysis of the sulfonic acid formed by sulfonation of m-xylene can be carried out in the presence of other sulfonic acids (117). A number of methods to separate the xylenes and ethylbenzene are based on this well known reaction (4, 18, 21, 36, 51, 53, 60, 117, 126). Apparently the method has not proven to be practical on a commercial scale, though its defects are not clear.

4. Tertiary-Butylation (94, 108, 119). Reaction of the compounds (p-xylene does not react readily) with isobutylene, separation of products, and then debutylation is another possibility. It has been used in the petroleum industry for some separations on a small scale. Application to this problem has already been studied (119).

II. Recovery of Compounds After Conversion of One to a Marketable Product

1. Dehydrogenation of ethylbenzene to styrene. Much work has been done on this dehydrogenation, especially in

the presence of other gases or vapors (7, 27, 71, 72). Better yields are obtained if the vapor pressure of ethylbenzene is below atmospheric. This can be effectively accomplished by dilution with CO_2, H_2O, C_6H_6, or xylenes (7, 27, 71, 72). These processes are all patented. Very good yields are reported with xylenes as the diluent and it is surprising that this has not been applied commercially. Separation of the ethylbenzene and styrene by distillation is not easy, however, and would be worse for m-xylene and styrene. Ethylbenzene and styrene can be separated by polymerization of styrene with benzoyl peroxide, fractional distillation to remove ethylbenzene, and depolymerization of the polystyrene (7). Other companies have studied this dehydrogenation in detail and the limited time available on this fellowship did not permit laboratory work along this line.

2. Conversion to oxygenated products. There is a good possibility that ethylbenzene can be converted to acetophenone in the presence of xylenes. Patents have been issued on this conversion with ethylbenzene itself (5, 6, 31). Marketing possibilities are the limiting factors here; the demand for acetophenone is not great. Liquid-phase oxidation to acids with common oxidizing agents is well known. Selective oxidation of xylenes in liquid phase using cobalt linoleate catalyst has also been studied (109).

3. Rearrangements and dealkylations. The literature in this field is very extensive. The xylenes can be isomerized thermally (30); m-xylene is the most stable one. Isomerization over various catalysts with (14) or without (48) addition of H_2 or H_2O is possible. In rearrangements over $AlCl_3$, the mixture approaches the composition of commercial xylene (90). Toluene is produced by passing benzene and xylenes over silica-alumina catalyst at 150 lb/in^2 pressure at 950 F. (52). Removal of the alkyl groups as light hydrocarbons is accomplished by passing the xylenes over HF-activated alumina catalyst (15). The short time available on this fellowship did not permit a study of this type.

EXTRACTIVE DISTILLATION

Theory

Extractive distillation can best be discussed in terms of relative volatilities. The relative volatility, αAB, of two components, A and B, in an ideal binary solution is:

$$\alpha AB = \frac{Y_A}{X_A} \bigg/ \frac{Y_B}{X_B}$$

where Y_A and Y_B are the mole fractions of A and B in the vapor and X_A and X_B are the mole fractions of A and B in the liquid. This expression can be arrived at as follows: In an ideal binary solution of A and B, the vapor pressure of each component can be expressed by Raoult's law:

$$\bar{p}_A = p_A X_A$$

$$\bar{p}_B = p_B X_B$$

where p is the vapor pressure of the pure compounds, $\bar{p}$ the partial pressure above the solution and X the mole fraction of the component in the liquid. The total pressure, P, above the solution is given by Dalton's law:

$$P = \bar{p}_A + \bar{p}_B$$

The relative volatility, αAB, is obtained as follows:

From Avogadro's law:

$$Y_A = \bar{p}_A/P$$

$$Y_B = \bar{p}_B/P$$

where Y_A and Y_B are mole fractions of A and B in the vapor. Combining these,

$$Y_A = p_A X_A/p$$

$$Y_B = p_B X_B/p$$

$$Y_A/Y_B = \frac{p_A X_A}{p_B X_B} = \alpha AB \frac{X_A}{X_B}$$

$$\alpha AB = \frac{Y_A}{X_A} \Big/ \frac{X_B}{Y_B}$$

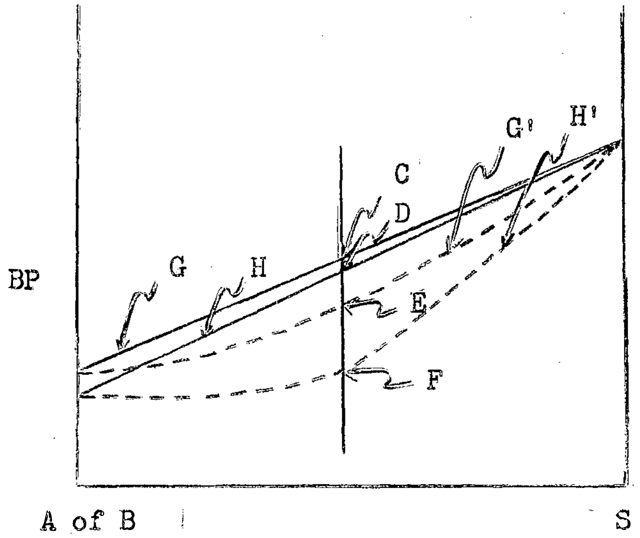
As an example, the αAB value of an azeotrope is unity; the components have the same volatilities with respect to each other and cannot be separated by ordinary distillation. Compounds having similar molecular configurations and nearly identical boiling points have an αAB value near unity and are therefore difficult to separate by distillation.

In extractive distillation, a nonideal system is created by addition of a solvent; in the resulting solution, the partial pressure relationships, and consequently the relative volatilities of the components to be separated, will be different. A slightly different value, the relative volatility in the presence of a certain mole fraction of solvent, $\alpha' AB$, is then used.

Methods of Selecting Suitable Solvent

An equilibrium still of the type described by Othmer (92) is the obvious way of getting at the αAB value. Here the mixture is introduced into the apparatus and it is run until equilibrium is obtained. Vapor and liquid samples are then analyzed and the αAB value calculated directly. In investigating the effectiveness of various solvents for extractive distillation purposes, the three components A, B, and solvent S are introduced and vapor and liquid samples taken and analyzed as before; however, now the value will be $\alpha'AB$, the relative volatility of A to B in the presence of a certain mole fraction of solvent. The mole fraction of solvent can then be varied to determine the optimum solvent-solute ratio to be used. Alternately, in order to reduce analytical problems, vapor-liquid data may be obtained with each component separately with the solvent and calculations made according to Othmer (93).

A qualitative measure of the degree of nonideality caused by addition of solvent to the solution and therefore of the effectiveness of the solvent for use in a particular extractive distillation may be obtained by determination of the boiling points of equivolume mixtures of each component and the solvent separately (123). This can be seen if reference to Figure 2 is made. Consider curves G and G'. G is the expected curve if A and solvent S form an ideal solution. G' is the curve obtained when there is a positive deviation from Raoult's law. The same is true of curves H and H' which show the behavior of component B and solvent. If distance EF is much greater than CD, then component A and solvent form a solution nearer ideality than B and solvent, and an alteration in relative volatilities of the two components is evident. A boiling-point difference of about 10^{o} is necessary for a solvent to be considered for use in extractive distillation. Laboratory-scale extractive distillations may be carried out as a further evaluation of a solvent. This is desirable only if a solvent shows promise by one of the previously described methods because of the much larger amount of work involved.



General Effect of Added Solvent on Relative Volatilities

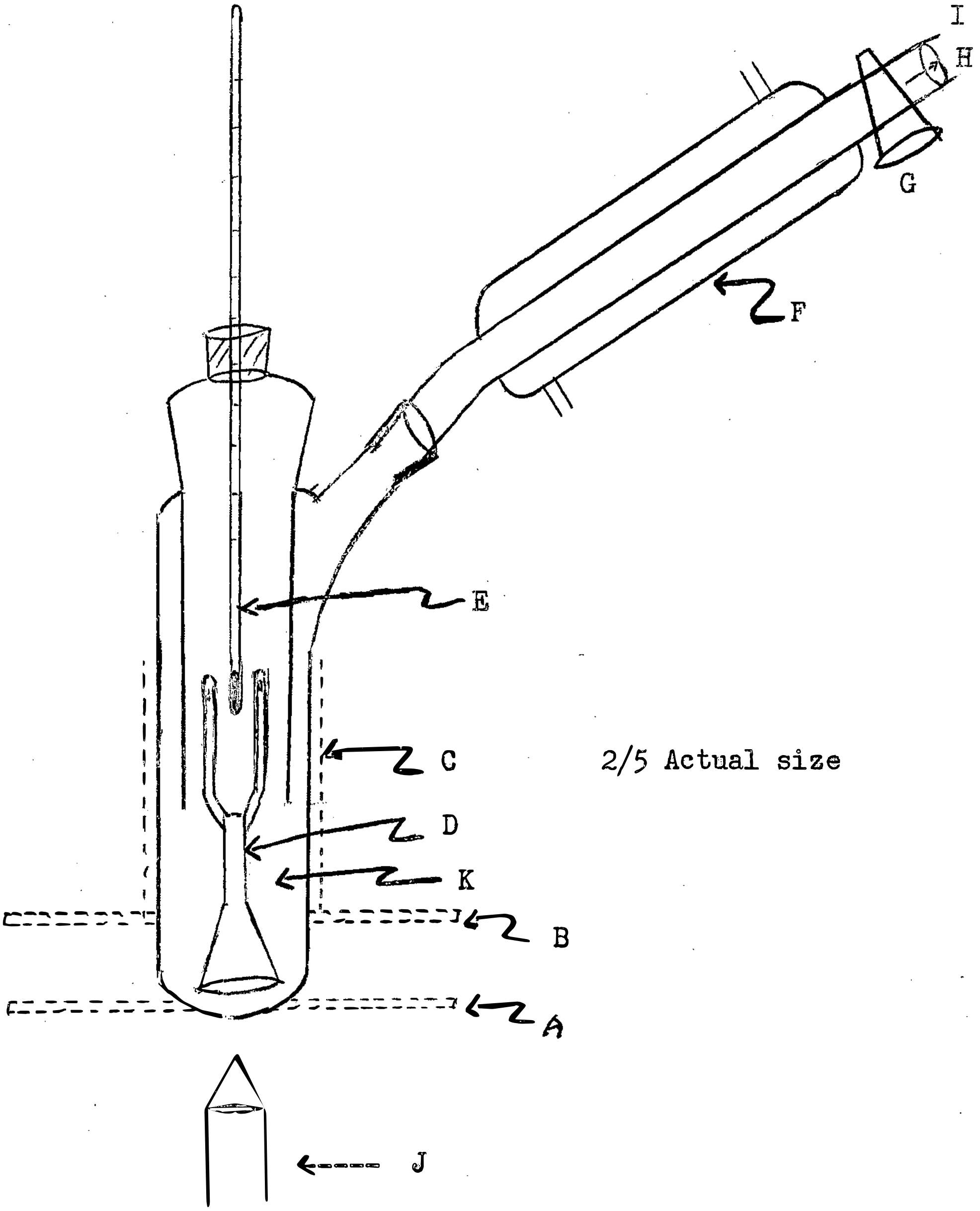
Figure 2

In practice, extractive distillation is carried out by introducing the third component into the distillation column near the top. As it runs down through the column, it selectively extracts one component, allowing the other to pass through. The solvent should therefore boil considerably higher than either component in order to avoid excessive vaporization and to make separation from the extracted component easy.

Apparatus and Experimental Procedure

The boiling-point method used by Weissberger (123), described on the previous page, was used in order to evaluate solvents for the extractive-distillation separation of m-xylene and ethylbenzene. Use of this simple method made possible the survey of a large number of possible extractants. The ordinary Brown boiling-point apparatus was used. A diagram of the complete apparatus as used in reduced-pressure determinations is shown in Figure 3. It was found to work satisfactorily over a wide temperature range, about 65° to 200° C.

For determinations at atmospheric pressure, G is opened and joint I disconnected from vacuum reservoir. A is an asbestos board 1/8" thick with a hole approximately one inch in diameter for the bottom of the apparatus to fit into. This allows heat from the Bunsen burner, J, to be concentrated in a small area on the bottom and causes a pumping action, liquid and vapor being pushed up through D to the thermometer bulb E. Since vapor and liquid are thrown onto the thermometer bulb simultaneously, superheating is minimized. B is another asbestos board 1/8" thick to prevent excessive heating of the upper parts of the apparatus, and C is asbestos insulation to minimize heat loss from the apparatus. F is a condenser and H a four-liter vacuum reservoir, evacuated by means of an aspirator pump. The experimental procedure for evaluating a solvent is as follows. Equal volumes, generally 30 ml. each, of one of the components (m-xylene or ethylbenzene) and the solvent are introduced into K. Heat is applied by means of a Bunsen burner until equilibrium is attained, which is manifested by a constant temperature on the thermometer. This temperature is recorded and the procedure is repeated with the other component and the solvent. If this temperature difference is about four degrees or less, the solvent is not promising and another one is tried in the same manner. If, however, this temperature difference is about four to five degrees or larger, different solvent-solute ratios are used, usually three to one and



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Boiling Point Apparatus

Figure 3

one to three in addition to the one-to-one ratio already used. The determinations are then run at several reduced pressures in order to see if a larger boiling point difference can be obtained. Pressures down to about 100 mm. were used in most cases; the lower value was sometimes limited by bumping and temperature fluctuations. In order to obtain readings at idential pressures, reduced-pressure determinations were made on the two binary systems by connecting two identical apparatuses to the same vacuum reservoir and operating them simultaneously.

Purity of Chemicals Used

The m-xylene used was from one of three sources: (1) Matheson Chemical Company reagent grade, b.p. 138.4° (751 mm.), n_D^{24} 1.4943; (2) the same, recovered by distillation from mixtures with solvents, with same physical properties as above; (3) Eastman Kodak Company reagent grade, b.p. 138.4° (743 mm.), n_D^{24} 1.4945.

The ethylbenzene was primarily Phillips Petroleum Company pure grade, 99 mole percent pure, b.p. 136.2° (751 mm.), n_D^{24} 1.4937.

Solvents were generally purified by simple distillation, if they were not reagent grade.

Results

Table III shows the boiling points of solvents and various equivolume binary mixtures of ethylbenzene and m-xylene with solvents at atmospheric pressure.

Table III

Alteration of Boiling Points by Solvents at Atmospheric Pressure

	Boiling Point, Degrees C.			
	Alone	+ Ethylbenzene	+ m-xylene	ΔT
n-Butyl borate	103.6 8 mm*	150.6	151.6	1.0
o-Chlorophenol	174.2	150.0	151.2	1.2
Stannic bromide#	202*	153.8	155.0	1.2
Aniline	183.4	150.0	151.4	1.4
Acetophenone	201.2	154.6	153.0	1.6
o-Bromotoluene	180.4	152.8	154.4	1.6
α-Chloropropionic acid	186*	147.4	149.2	1.8
Methyl salicylate	222.4	157.6	159.4	1.8
Acetamide	217.0	139.2	141.2	2.0
Tri-n-butylamine	216.5	150.6	152.6	2.0
Phenol	180.8	148.0	150.2	2.2
Propionic anhydride	167.0	144.0	146.2	2.2
2-Benzyloxyethanol	256*	153.0	155.2	2.2
Benzylamine	181.0	151.6	153.8	2.2
o-Toluidine	196.4	154.4	156.6	2.2
o-Nitrotoluene	221.2	157.4	159.8	2.4
Furfuryl alcohol	169.5*	140.4	142.8	2.4
Dimethylaniline	192.0	155.2	157.6	2.4
1,2,4-Trichlorobenzene	212.6	159.2	161.6	2.4
Benzonitrile	189.6	151.8	154.4	2.6
m-Cresol	201.0	152.6	155.2	2.6

	Boiling Point, Degrees C.			
	Alone	+ Ethylbenzene	+ *m*-xylene	ΔT
Benzaldehyde	178.6	150.0	152.6	2.6
Benzoic acid	238	157.2	159.8	2.6
Benzyl alcohol	203.5	151.2	153.8	2.6
p-Chlorophenol	217*	157.6	160.2	2.6
Quinoline	237.1	158.4	161.0	2.6
α,α,α-Trichlorotoluene	220.7*	158.0	160.6	2.6
Phosphorus tribromide#	175.3	148.6	151.2	2.6
o-Dichlorobenzene	179.0	152.6	155.4	2.8
Salicylaldehyde	193.0	154.4	157.2	2.8
2,4-Dichlorophenol	208.14	157.6	160.4	2.8
Phenylhydrazine	243.5*	152.8	155.6	2.8
o-Chloroaniline	210.5*	156.0	158.8	2.8
p-Ethylphenol	-----	154.2	157.0	2.8
Cyclohexanecarboxylic acid	232*	153.6	156.6	3.0
2-Octanol	178.4	147.0	150.0	3.0
2-Octanone	169.0	147.8	150.8	3.0
Antimony trichloride-hydrogen chloride))	-----	171.4-.8	174.4-.8	3.0
Ethyl benzoate	211.4	156.2	159.4	3.2
1,1,2-Tribromoethane	187.8*	154.0	157.4	3.4
Chloroacetic acid	188.4	145.4	148.8	3.4
Nitrobenzene	209.6	155.6	159.2	3.6
Ethanolamine	170.4	128.2	131.8	3.6
p-Nitrotoluene	237.7*	158.2	161.4	3.6

	Boiling Point, Degrees C.			
	Alone	+ Ethylbenzene	+ *m*-xylene	ΔT
Diphenyldichlorosilane	280-306	154.8	158.4	3.6
Maleic anhydride	202*subl.	145.0	148.0	3.8
Arsenous bromide-hydrogen chloride))	-----	161.4	165.2	3.8
Chloromaleic anhydride	196.3*	149.8	153.8	4.0
Antimony tribromide#	281.4	161.6	165.8	4.2
Arsenous bromide#	221*	159.4	164.2	4.8
Antimony trichloride	220.2*	167.0	173.2	6.2

*Literature value

))The solvent was mixed with the hydrocarbon and anhydrous HCl bubbled through the mixture 5-7 minutes.

#Synthesized from the elements since not on hand.

Table IV shows the boiling points of hydrocarbons with various additives at several pressures. A plot of the arsenous bromide and antimony bromide data appears in Figure 4.

Table IV

Alteration of Boiling Points by Additives at Various Pressures

Additive	Composition		Boiling Point, Degrees C.				Pressure, mm.
	Additive, ml.	Hydrocarbon, ml.	Alone	+ Ethylbenzene	+ m-Xylene	ΔT	
Stannic chloride	30	30	114.1*	84.0	84.4	0.4	246
				97.6	98.4	0.8	390
				119.6	120.8	1.2	748
Titanium tetrachloride	30	30	136.4*	66.5	67.4	0.9	82
				86.0	87.0	1.0	163
				112.0	113.0	1.0	387
				124.0	124.8	0.8	550
Aluminum** chloride	0.2 g.	30		120.8	123.6	2.8	494
			182.7*	135.8	138.6	2.8	752
Arsenous bromide	25	25		86.6	90.0	3.4	86
				97.4	101.2	3.8	123
				113.0	117.0	4.0	203
				129.8	133.6	3.8	334
				142.0	145.8	3.8	463

	Composition		Boiling Point, Degrees C.				
Additive	Additive, ml.	Hydrocarbon, ml.	Alone	+ Ethylbenzene	+ $\underline{m}$-Xylene	ΔT	Pressure, mm.
Arsenous				148.8	153.2	4.4	561
bromide				153.2	157.8	4.6	628
			221	160.0	165.0	5.0	740
Antimony	20	20		97.0	102.4	5.4	126
bromide				116.4	122.[illegible]	5.6	231
				130.0	135.4	5.4	341
				141.6	147.0	5.4	472
				146.5	151.5	5.0	539
				152.2	157.0	4.8	623
			281-4	161.6	165.8	4.2	748
Furfural	25	25		83.6	85.8	2.2	125
				108.4	110.6	2.2	292
				122.4	124.4	2.0	444
				133.8	135.8	2.0	617
			161.7	141.0	143.0	2.0	750
Chloranil**	5g.	30		138.0	141.6	3.6	752

Additive	Composition		Boiling Point, Degrees C.				Pressure, mm.
	Additive, ml.	Hydrocarbon ml.	Alone	+ Ethylbenzene	+ m-Xylene	ΔT	
Maleic anhydride	30	30		85.6	89.6	4.0	130
				100.6	104.6	4.0	212
				114.0	118.0	4.0	322
				127.8	131.8	4.0	477
				135.6	139.4	3.8	586
			202 subl.	145.2	149.0	3.8	747

*Literature value

**Quantity of additive limited by solubility and reaction on heating.

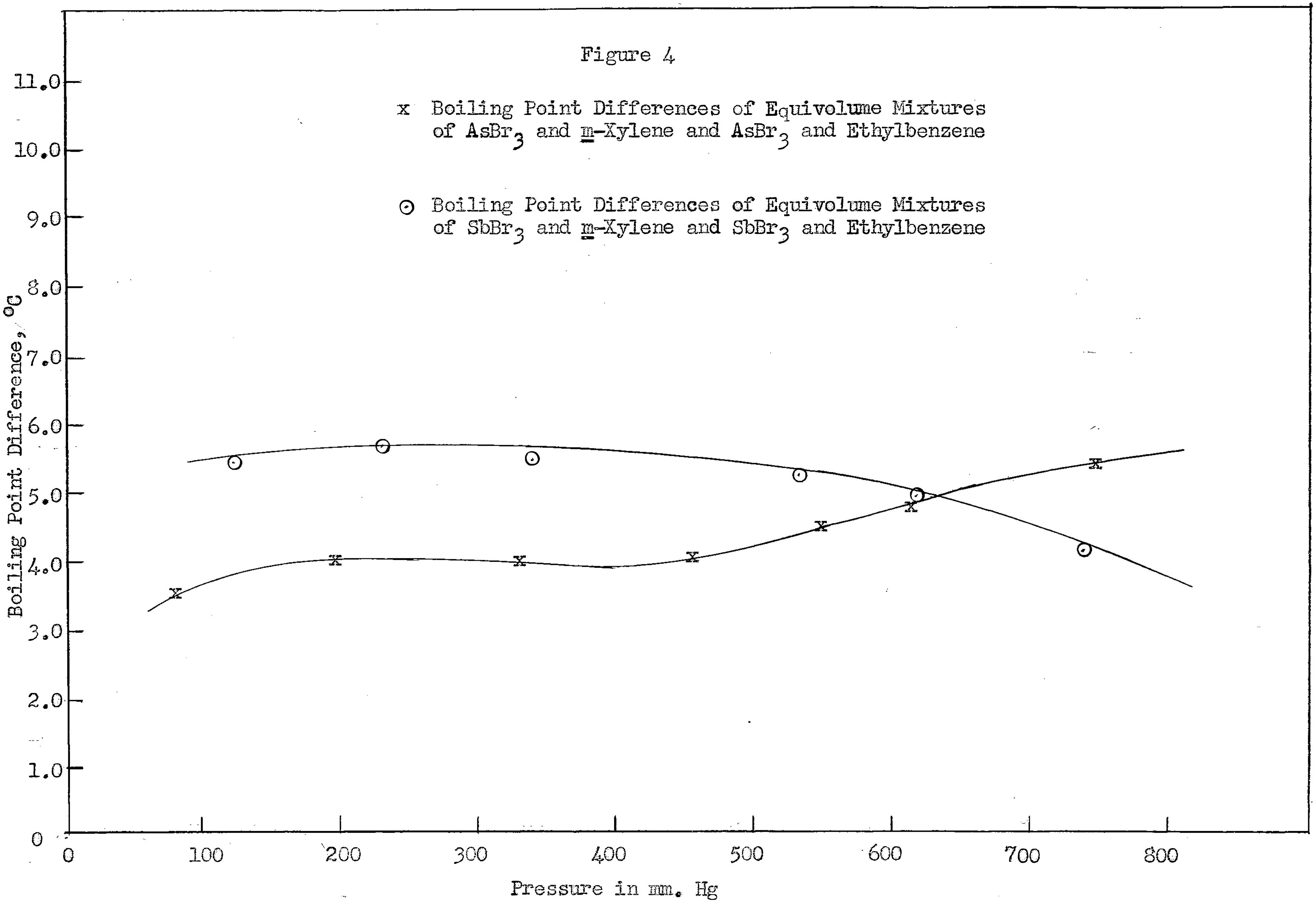


Figure 4

x Boiling Point Differences of Equivolume Mixtures of AsBr3 and m-Xylene and AsBr3 and Ethylbenzene
⊙ Boiling Point Differences of Equivolume Mixtures of SbBr3 and m-Xylene and SbBr3 and Ethylbenzene
Boiling Point Difference, °C
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
0
100
200
300
400
500
600
700
800
Pressure in mm. Hg

Table V shows the boiling points of antimony trichloride-hydrocarbon systems at several pressures and different solvent-hydrocarbon ratios. A plot of these data appears in Figure 5.

Table V

Alteration of Boiling Points by Antimony Trichloride

Boiling Point, °C Antimony chloride plus ethylbenzene	Boiling Point, °C Antimony chloride plus m-xylene	ΔT	Antimony chloride-hydrocarbon ratios by volume	Pressure, mm.
69.6	73.4	3.8	1:3	60
82.4	86.2	3.8	1:3	91
93.8	97.8	4.0	1:3	144
113.6	117.8	4.2	1:3	271
124.2	128.6	4.4	1:3	384
136.2	140.6	4.4	1:3	535
149.8	154.2	4.4	1:3	742
86.2	93.8	7.6	1:1	60
96.6	103.6	7.0	1:1	88
113.0	119.4	6.4	1:1	154
123.2	129.8	6.6	1:1	209
138.0	144.6	6.6	1:1	327
152.2	158.2	6.0	1:1	485
169.0	174.8	5.8	1:1	736
100.4	111.0	10.6	3:1	44
133.8	144.2	10.4	3:1	153
148.6	158.4	9.8	3:1	244
162.4	171.4	9.0	3:1	366

Boiling Point, °C Antimony chloride plus ethylbenzene	 Antimony chloride plus m-xylene	ΔT	Antimony chloride-hydrocarbon ratios by volume	Pressure, mm.
176.6	184.2	7.6	3:1	534
190.4	195.4	5.0	3:1	748

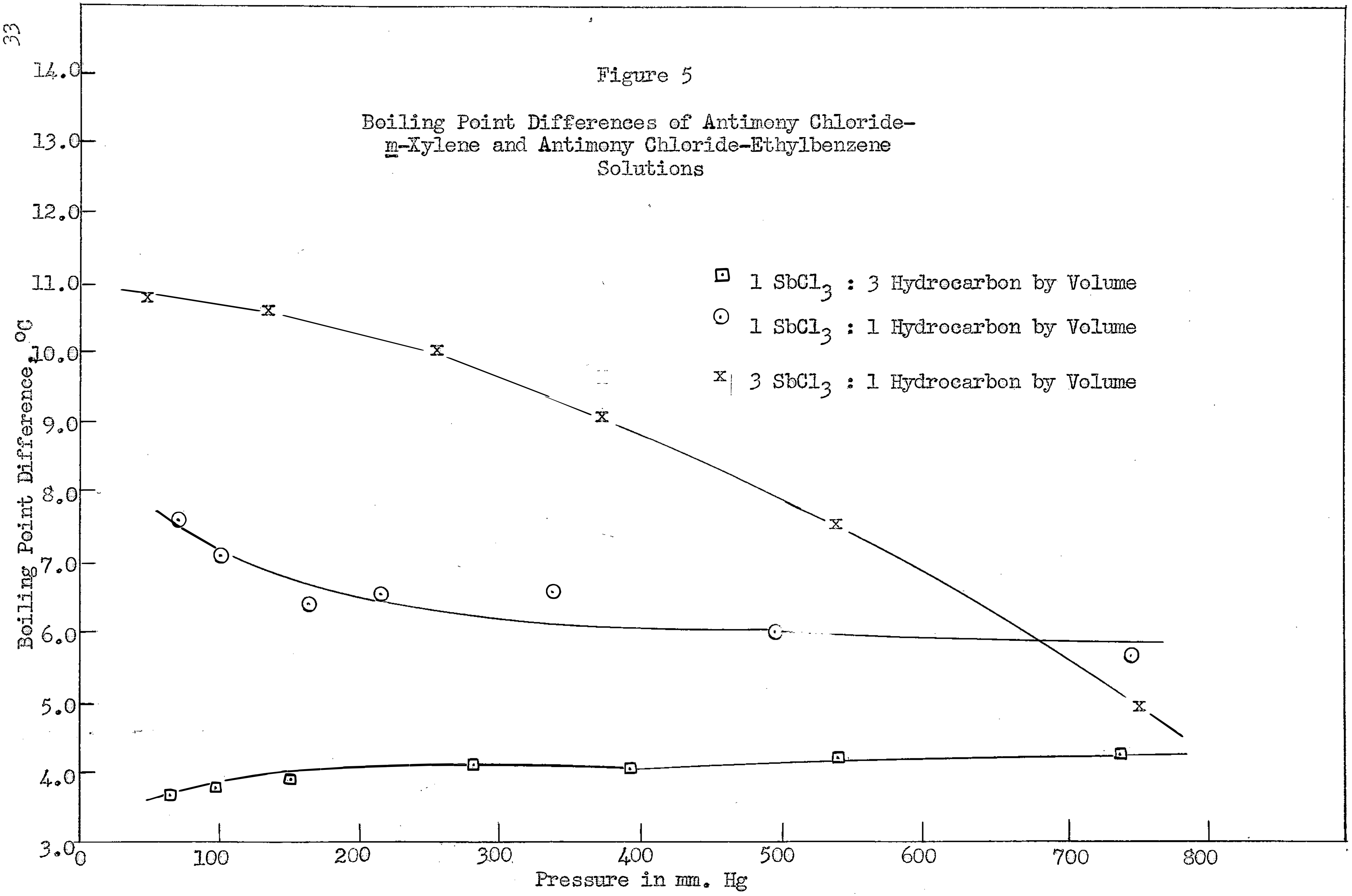


Figure 5

Boiling Point Differences of Antimony Chloride-m-Xylene and Antimony Chloride-Ethylbenzene Solutions

Discussion

As previously stated, a boiling-point difference of about 10° C between the m-xylene-solvent solution and the ethylbenzene-solvent solution is necessary for a solvent to be potentially useful as an extractant. Of the solvents appearing in Table III, antimony chloride, antimony bromide, and arsenous bromide give the greatest boiling-point differences. The solvents were selected to represent the major classes of organic compounds and since none of those in Table III gave good results, none was investigated further. Three other organic compounds were tried; these appear in Table IV. The boiling-point differences in the maleic anhydride and furfural systems were not enhanced at reduced pressures and these extractive solvents were not further considered.

Inorganic solvents were selected primarily on the basis of their physical properties, as most inorganic compounds are sufficiently ionic to have a boiling point too high to be of use here. This left only a small group from which to choose when unstable and rare compounds were eliminated.

The limited success with halides of elements of group V of the periodic table led to investigation of other covalent halides shown in Table IV. Of these only antimony bromide was at all promising, and it and the arsenous bromide were studied at reduced pressure (Table IV and Figure 4) with rather poor results. The success of the $HF-BF_3$ hydrocarbon systems in liquid-liquid extraction (section IB2 of this thesis) suggested the trial of the antimony chloride- and arsenous bromide-hydrogen chloride systems listed in Table III.

These metal halides have rather weak Lewis acid properties. McCaulay (81) did not discuss the mechanism by which the HF-BF_3 extraction took place other than that the interaction between hydrocarbon and BF_3 was apparently instantaneous. He indicated that the equilibrium in this system apparently is shifted far to the left;

$$HF + BF_3 \rightleftharpoons H^+ + BF_4^-$$

it is not known what part HF plays in the complexing mechanism. By analogy to this, an increase in boiling-point differences when HCl is added to the antimony chloride and arsenous bromide systems would possibly be expected. However the opposite effect was observed. No explanation is obvious but some sort of attraction between HCl and $SbCl_3$ or $AsBr_3$ (possibly an increase in covalence of the metals by complex formation) resulting in alteration of their acidic properties toward hydrocarbons is probable.

The antimony chloride-aromatic hydrocarbon systems were studied rather thoroughly (Table V and Figure 4). The largest boiling-point differences were obtained at low pressures and high halide-to-hydrocarbon ratios. The results with antimony chloride systems in principle verify patents (88, 91) which claim this solvent for the separation of ethylbenzene and the xylenes. However, results with the antimony chloride are not readily explainable. Some sort of selective Lewis acid-base type complex is possible; however Nixon, et al (88) do not believe this is the case under extractive distillation conditions. Solid and liquid-phase complexes between aromatics and these halides are well known (see section IB2, historical part of this thesis) but whether this fits into the results here is debatable. Some of the other inorganic compounds tested, e.g., aluminum chloride and titanium chloride, also complex with these hydrocarbons and they did not prove useful. Possibly antimony chloride has just the right degree of acidity toward this mixture to cause unusual results. At any rate, findings here and those of Chu, Kharbanda, Brooks, and Wang (19) do not suggest further work on extractive distillation for this separation.

SOLID COMPLEX FORMATION

Theory

Many methods may be used to study solid and liquid molecular complexes. The most important of these have been discussed in section IB2 of the historical part of this thesis. The one used here is described below.

Complex formation of the type found between antimony chloride and aromatic hydrocarbons can be represented by the general equation:

$$A_{(s)} + xB_{(g)} = AB_{x\ (s)}$$

The thermodynamic dissociation constant for the above reaction may be written:

$$K_{dissoc.} = \frac{a_{A(s)} \cdot a^{x}_{B(g)}}{a_{AB_x\ (s)}}$$

For a pure solid the activity is constant and if the pure solid is chosen as the standard state, the constant activity is set equal to unity. This permits us to write the preceding equation as:

$$K_{dissoc.} = a^{x}_{B(g)}$$

The standard state for a gas at any given temperature is taken as the state in which the fugacity is equal to unity, $f = 1$. On this basis, the activity of any gas becomes equal to the fugacity:

$$A = \frac{f}{f^{o}} = \frac{f}{1} = f$$

For an ideal gas the fugacity is equal to the pressure. Since however any gas can be brought to an ideal state by reducing the pressure to zero, in general:

$$f = P \text{ as } P \rightarrow 0$$

At relatively low pressures, therefore, pressure may be substituted for activity and we have:

$$K_{dissoc.} = P_B^x$$

Measurement of the vapor pressure of a molecular complex then determines the dissociation constant.

The heat of dissociation may be derived from the integrated form of the Clausius-Clapeyron equation:

$$\log_{10} P = \frac{-\Delta H}{2.303R} \cdot \frac{1}{T} + C$$

It is assumed in deriving this equation that the vapor behaves as an ideal gas; this is a good approximation in view of the low vapor pressures measured here. If $\log_{10} P$ is plotted vs $1/T$, a straight line results with the slope, m, equal to $-\Delta H/2.303R$. From this the heat of dissociation is given by:

$$\Delta H = -2.303\ R\ m$$

The heat of dissociation calculated from this is for the temperature range used in making the vapor pressure measurements.

The free energy change in the standard state for reaction 1 may be calculated from the equation:

$$\Delta F^{o} = -RT \ln K$$

where K is the thermodynamic equilibrium constant as before.

The vapor pressure of each complex may be expressed at any temperature within the experimental range of measurements by means of following equation, where A and B are constants:

$$\log_{10} P = -\frac{A}{T} + B$$

Experimental Procedure, Apparatus, and Results

I. Preparation and Isolation of Complexes.

1. Experimental Procedure. A preliminary study of these complexes of antimony chloride with m-xylene and ethylbenzene was made by preparation and isolation of the solids. They were prepared by heating an excess of the hydrocarbon with the halide. After the complex crystallized, it was filtered out and pressed dry between filter papers. Determination of the mole ratio of antimony chloride to hydrocarbon was accomplished by dissolving a weighed sample of the complex in 6 N HCl and titrating with standard potassium bromate to the methyl orange end point (118). This method of study is unreliable because of the instability of the complexes. Contact with moisture hydrolyzes the halide; furthermore, decomposition to hydrocarbon and halide occurred even when the complex was stored in tightly stoppered bottles.
2. Results. Table VI gives the composition of antimony chloride-hydrocarbon complexes as determined by the method described above.

II. Measurement of Vapor Pressures of Complexes.

1. Experimental Procedure. The apparatus and procedure used in measuring the vapor pressures of these antimony chloride complexes is essentially the one described in detail by Harper (42). The design is advantageous in that it permits foreign gases easily to be flushed from the system, and it makes absolute vapor presure measurements easier by comparison

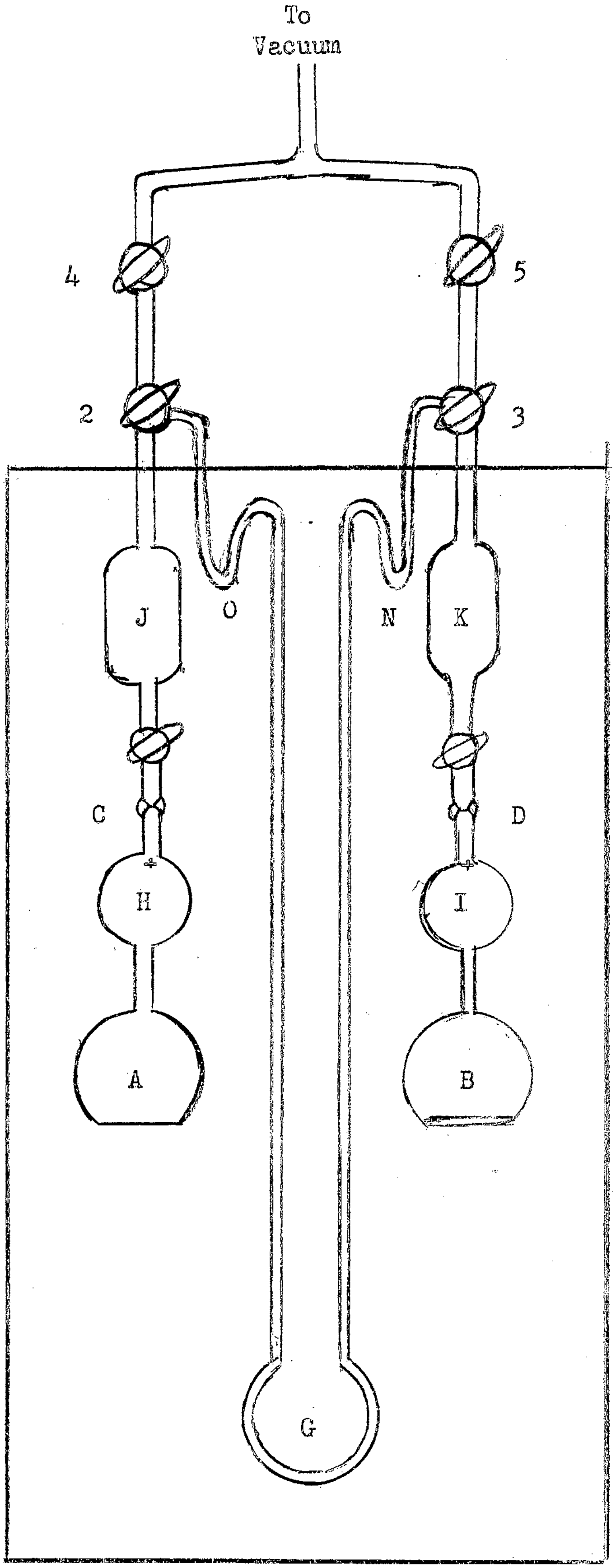
Table VI

Properties of Complexes Isolated by Filtration and Drying

	Compn. of Initial Mixture	Nature of Complex	% Antimony Chloride in Complex	Mole Ratio of Antimony Chloride to Hydrocarbon
(1)	10 ml. *m*-xylene + 20 ml. antimony chloride	Very hard Slight redish color	88.5-89.7	$\frac{3.59}{1}$ to $\frac{4.04}{1}$
(2)	10 ml. ethylbenzene + 20 ml. antimony chloride	Smaller quantity than above; same color	96.6-97.0	$\frac{13.3}{1}$ to $\frac{15.1}{1}$
(3)	10 ml. *m*-xylene + 10 ml. antimony chloride	Same as in 1; smaller quantity	88.4-91.3	$\frac{3.55}{1}$ to $\frac{4.86}{1}$
(4)	10 ml. ethylbenzene + 10 ml. antimony chloride	Very small quantity; same color	80.6-82.4	*

* Not calculated because analytical data believed inaccurate.

of the unknown pressure to an accurately known one. A schematic drawing is shown in Figure 6. The bath temperature was regulated to ± 0.1 C. Temperature measurement was made with a thermometer graduated to 0.1°, which had been compared to a Bureau of Standards thermometer. H, I, J, K, O, and N are traps to prevent the contents of flasks A and B from being carried to manometer G. Stopcocks 2 and 3 permit flasks A and B



Vapor Pressure Apparatus
Figure 6

to be connected either to the vacuum lines or to manometer G. Stopcocks 4 and 5 are auxiliary ones to prevent leakage from the rest of the system to the vacuum line in case stopcocks 2 and 3 develop leaks. Extreme difficulty was experienced in preventing this leakage, although the stopcocks developed leaks only after several hours' operation and then only to the vacuum line, not to the outside of the system. Many lubricants were tried, one being a hydrocarbon-resistant preparation described by Meloche and Frederick (80). This preparation absorbed water readily and produced a vapor pressure in the system. The problem was solved by selecting new stopcocks, using Dow Corning high vacuum silicone lubricant, and rather strong clamps on each of the stopcocks. In order to measure the vapor pressure of a complex of benzene and antimony chloride, for instance, a solution of the halide in benzene is placed in A. Pure benzene is placed in B. Stopcocks 2 and 3 are turned and vacuum (rotary vacuum pump) cautiously applied to A and B. The evaporation of benzene flushes out all air from the system during several such evacuations. If the system is free from air, a constant vapor pressure difference between A and B is noted by measuring the manometer levels with a cathetometer (readable to 0.1 mm.). This difference is the difference in vapor pressure of pure benzene and a saturated solution of antimony chloride in benzene. On further evacuation, another constant vapor pressure difference, different from the first, is eventually noted. This represents the vapor pressure difference between solid hydrocarbon complex and benzene. Further evacuations were made on each of the complexes to determine if more than one constant vapor pressure, indicating more than one complex ratio between antimony chloride and hydrocarbon, exist. However only one constant vapor pressure was found in each case. Since the vapor pressure of benzene is known at each temperature, that of the complex can be calculated. This can be used to determine $\Delta H_{dissoc.}$ as previously described. The mole ratio of hydrocarbon to halide may be obtained by placing a known weight of antimony trichloride in A, and evacuating until the sudden pressure change indicates that the complex has just been reached. The stopcock above C is closed and A is weighed. The gain in weight is the weight of benzene complexed with the antimony chloride.

2. Vapor Pressures of Reference Liquids.

These were calculated at each temperature from the following equations where t is the temperature in degrees C (59).

$$\log_{10} P \text{ for benzene} = 6.89745 - \frac{1206.350}{220.237 + t}$$

$$\log_{10} P \text{ for toluene} = 6.95334 - \frac{1343.943}{219.377 + t}$$

Vapor pressures at the temperatures employed calculated from the above equations appear in Table VII.

3. Methods of Calculation.

The slopes of the lines obtained by plotting $\log_{10} P$ vs $1/T$ were calculated by the method of least squares (103). The method is much more accurate than obtaining the slopes graphically. The vapor pressure data of each system were fitted to equations appearing in the following section by the method of averages (23).

Vapor Pressures of Benzene and Toluene

T, °C	P for benzene, mm.	P for toluene, mm.
20.0	74.97	21.83
20.4	------	22.30
22.0	------	24.30
25.0	94.80	28.44
28.0	------	33.16
30.0	119.1	36.66
32.0	------	40.46
34.0	------	44.59
35.0	148.3	------
40.0	183.5	------
45.0	225.9	------
50.0	272.8	------

4. Purity of Chemicals.

The antimony chloride used in formation of the complexes for vapor pressure measurements was Baker's reagent grade. m-Xylene and ethylbenzene purities were described on page Benzene and toluene were reagent grade, dried over sodium.

5. Results.

A. The Antimony Chloride - Benzene System. Experimental data for this system are tabulated below. A plot appears in Figure 7.

T, °K	1/T, °K	Manometer level difference, mm.	Pressure of complex, mm.	$\log_{10}$ P (atm)
293.2	0.00341	6.86	6.4	-2.0746
298.2	0.00335	8.77	7.1	-2.0295
303.2	0.00330	10.97	9.4	-1.9076
308.2	0.00324	13.54	12.9	-1.7703
313.2	0.00319	16.43	19.2	-1.5976
318.2	0.00314	20.00	25.9	-1.4675
323.2	0.00309	23.42	36.8	-1.3150

Reference liquid: Benzene

Slope of line : -2.76

$\Delta H_{dissoc.}$: 12.6 kcal./mole

Mole ratio of antimony chloride to benzene at 25° : 2.07.

Vapor pressure of complex as a function of temperature:

$$\log_{10} P = \frac{-2820}{T} + 7.407$$

B. The Antimony Chloride-Toluene System.

Experimental data for this system are tabulated below. A plot appears in Figure 8.

T, °K	1/T, °K	Manometer level difference, mm.	Pressure of complex, mm.	$\log_{10}$ P (atm)
298.2	0.00335	21.9	6.5	-2.0679
303.2	0.00330	28.2	8.5	-1.9514
308.2	0.00324	37.3	10.6	-1.8555
313.2	0.00319	45.9	13.2	-1.7603
318.2	0.00314	60.4	13.8	-1.7410

T, °K	1/T, °K	Manometer level difference, mm.	Pressure of complex, mm.	$\log_{10}$ P (atm)
323.2	0.00309	73.8	18.8	-1.6066
328.2	0.00305	89.5	22.7	-1.5248
333.2	0.00300	109.9	30.6	-1.3951

Reference liquid: Toluene

Slope of line : -1.57

$\Delta H_{dissoc.}$: 7.2 kcal./mole

Mole ratio of antimony chloride to toluene at 25°: 2.24

Vapor pressure of complex as function to temperature:

$$\log_{10} P = \frac{-1830}{T} + 4.088$$

C. The Antimony Chloride-Ethylbenzene System.

Experimental data for this system are tabulated below. A plot appears in Figure 9.

T, °K	1/T, °K	Manometer level difference, mm.	Pressure of complex, mm.	$\log_{10}$ P (atm)
293.6	0.00341	18.7	3.6	-2.3245
298.2	0.00335	23.3	5.1	-2.1732
303.2	0.00330	30.9	5.8	-2.1174
305.2	0.00328	33.2	7.3	-2.0175

Reference liquid: Toluene

Slope of line : -2.12

$\Delta H_{dissoc.}$: 9.7 kcal./mole

Mole ratio of antimony chloride to ethylbenzene: not determined.

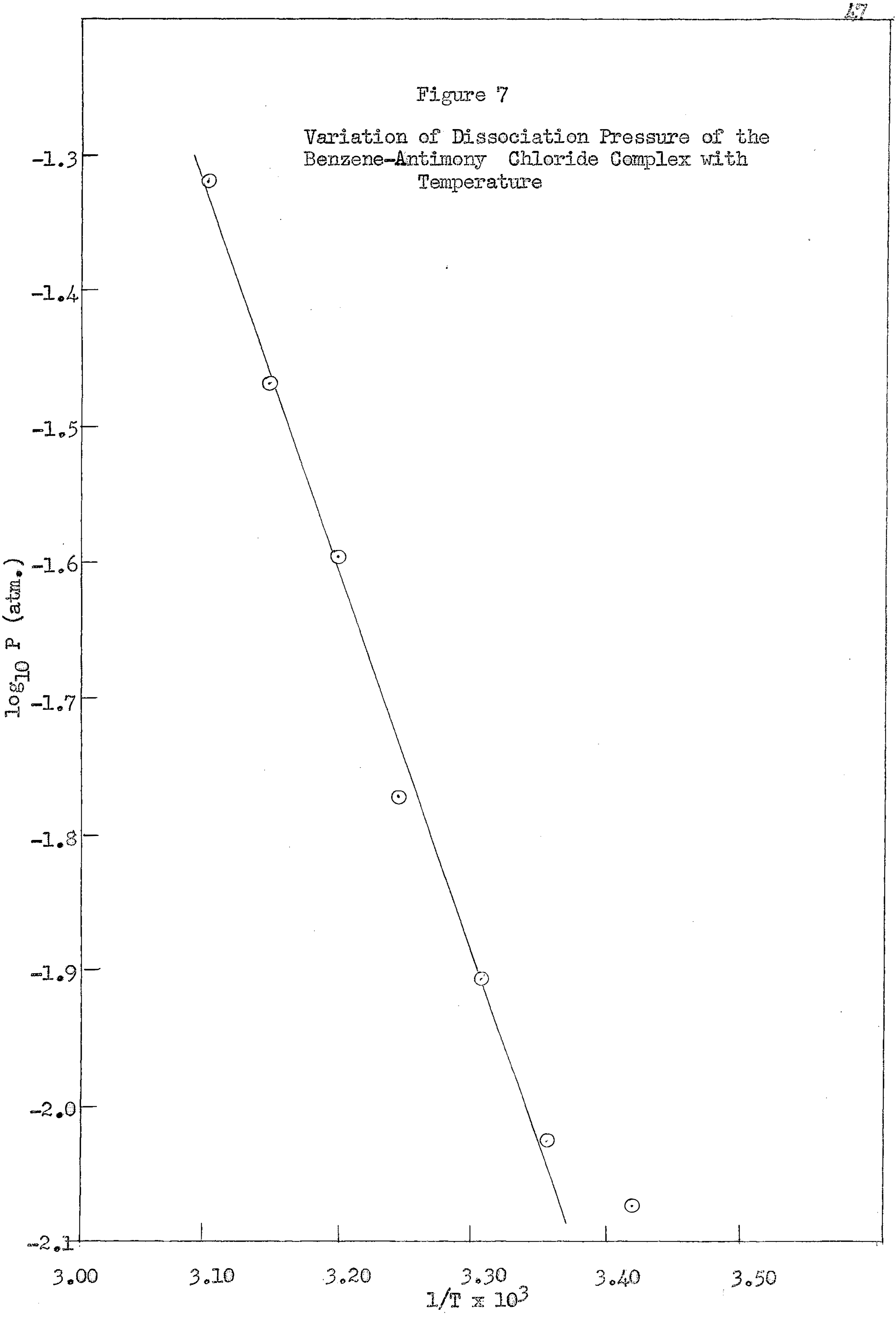
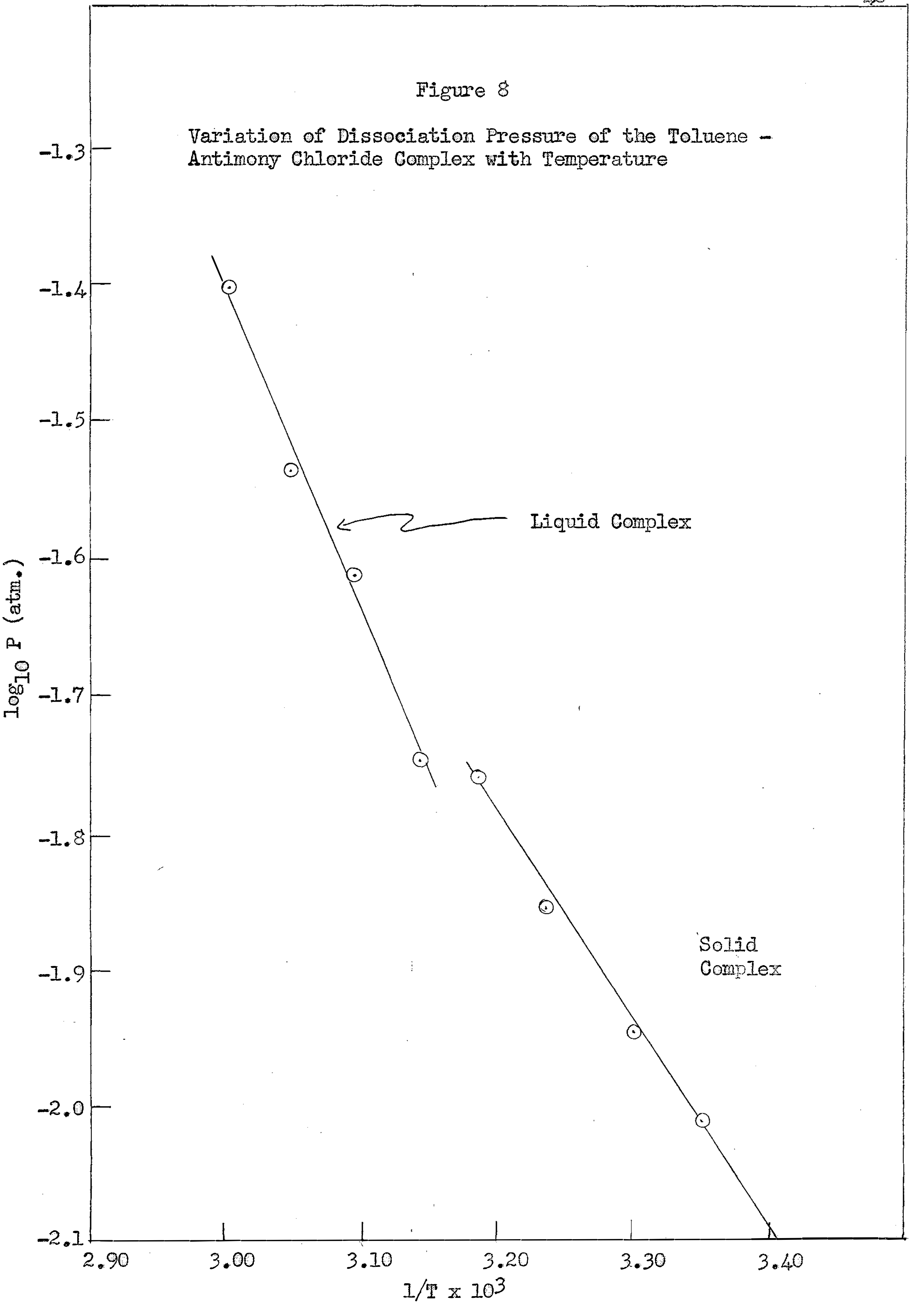


Figure 7

Variation of Dissociation Pressure of the Benzene-Antimony Chloride Complex with Temperature

Figure 8

Variation of Dissociation Pressure of the Toluene - Antimony Chloride Complex with Temperature



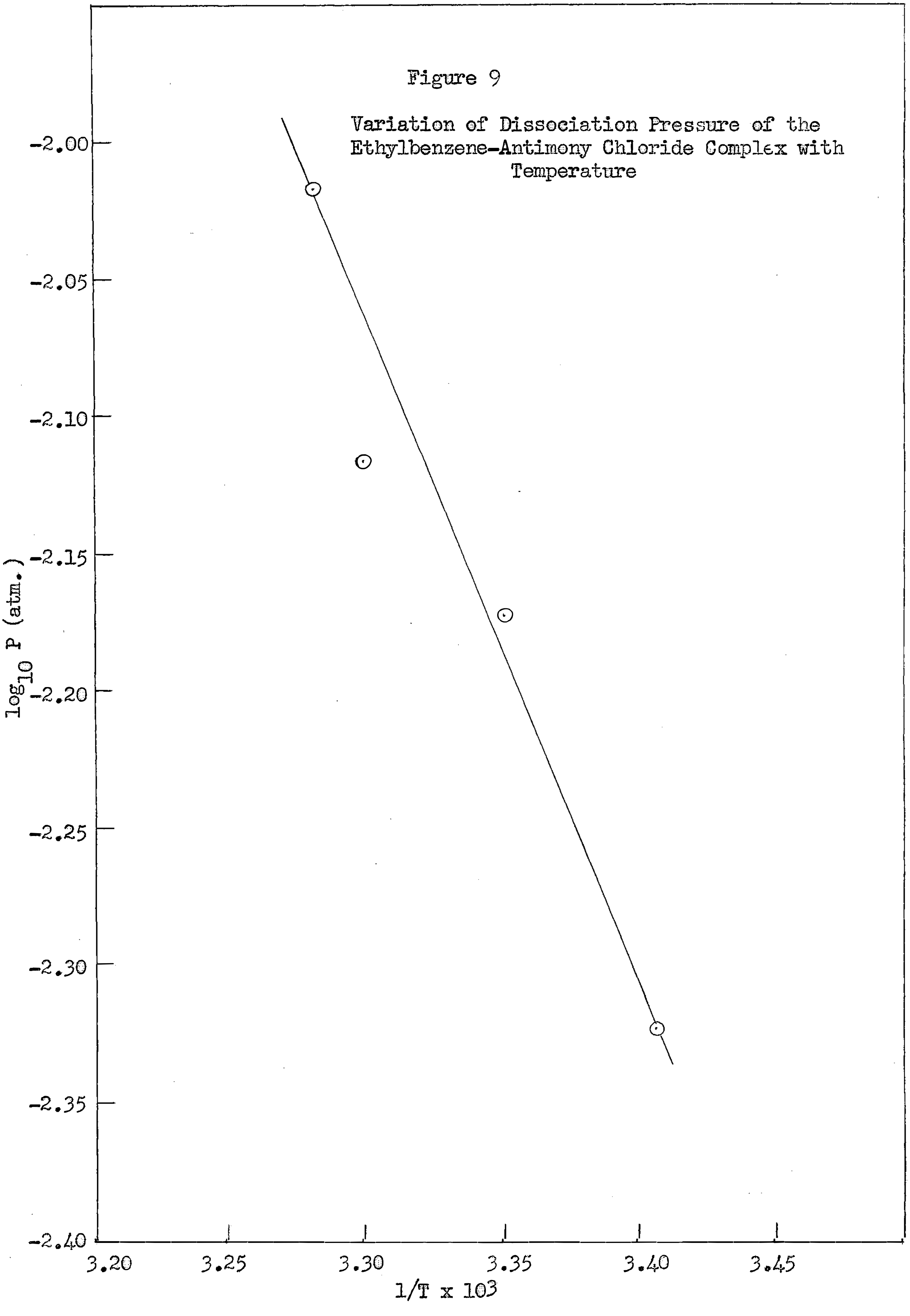


Figure 9

Variation of Dissociation Pressure of the Ethylbenzene-Antimony Chloride Complex with Temperature

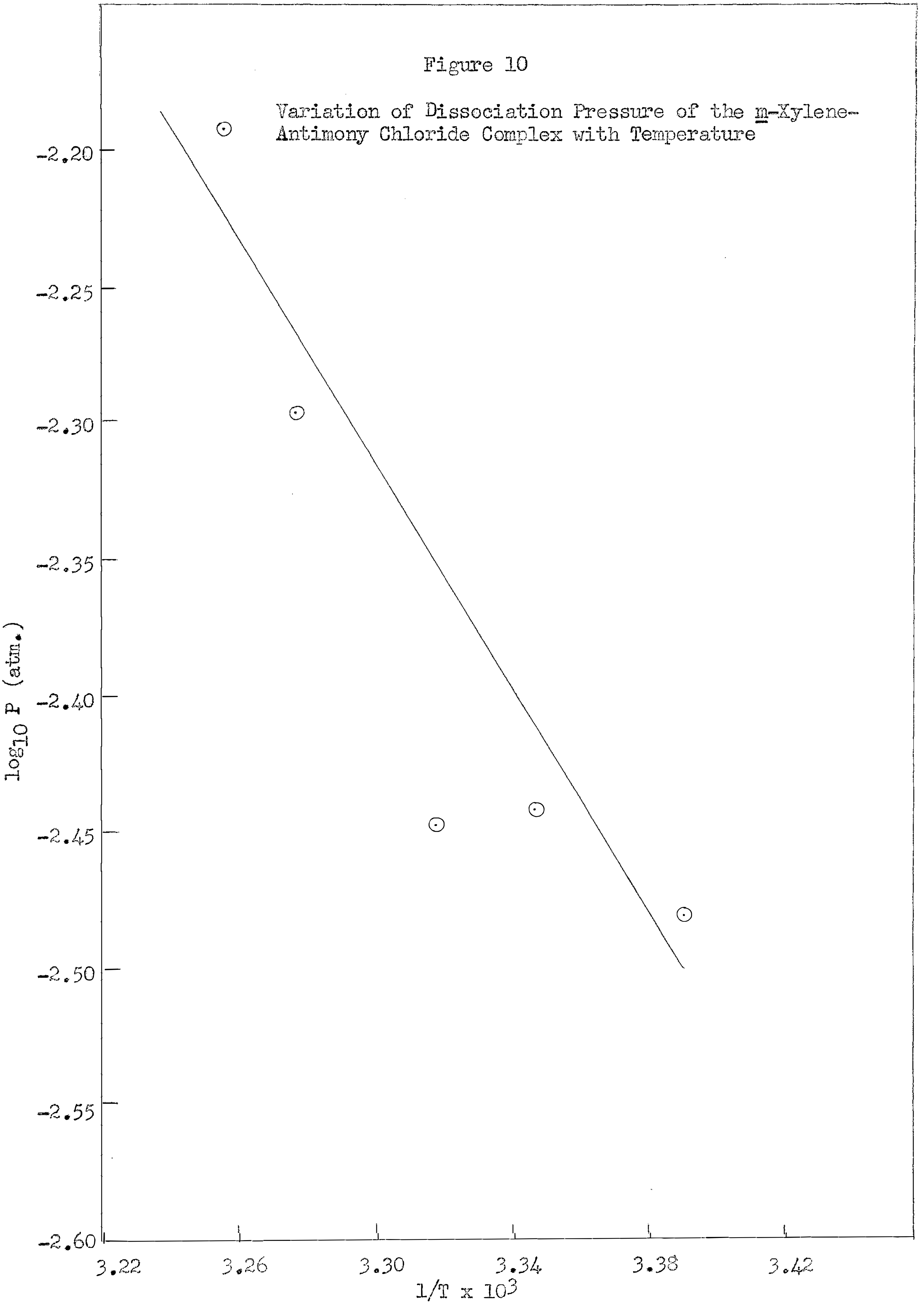


Figure 10
Variation of Dissociation Pressure of the m-Xylene-Antimony Chloride Complex with Temperature
-2.20
-2.25
-2.30
-2.35
-2.40
-2.45
-2.50
-2.55
-2.60
log10 P (atm.)
3.22
3.26
3.30
3.34
3.38
3.42
1/T x 10³

Vapor pressure as function of temperature:

$$\log_{10} P = \frac{-2020}{T} + 4.565$$

D. The Antimony Chloride - *m*-Xylene System.

Experimental data for this system are tabulated below.

A plot appears in Figure 10.

T, ^{o}K	1/T, ^{o}K	Manometer level difference, mm.	Pressure of complex, mm.	$\log_{10}$ P (atm)
295.2	0.00339	31.8	2.5	-2.4829
298.2	0.00335	25.6	2.8	-2.4337
301.2	0.00332	30.5	2.7	-2.4495
305.2	0.00328	36.7	3.8	-2.3010
307.2	0.00326	39.8	4.8	-2.1996

Reference liquid: Toluene

Slope of line : -2.07

$\Delta H_{dissoc.}$: 9.5 kcal./mole

Mole ratio of antimony chloride to *m*-xylene: not determined.

Vapor pressure as a function of temperature.

$$\log_{10} P = \frac{-2080}{T} + 4.816$$

DISCUSSION

The study of these complexes by isolation and analysis was only preliminary and for the reason already mentioned, i.e., instability of the complexes, no more work of this type was done. The analytical results are certainly untrustworthy. This may be owing to: (1) insufficient removal of hydrocarbon from the complex, (2) dissociation of the complex and loss of hydrocarbon, or (3) hydrolysis by moisture in the air.

The vapor pressure studies were undertaken to determine relative stabilities of the several complexes. These compounds have been known for many years; however, nothing but phase rule studies had been made on the solid complexes. It was hoped that the complex derived from one of the hydrocarbons (m-xylene or ethylbenzene) would have a quite different vapor pressure or heat of dissociation than the other and that some sort of separation scheme could be built around this. Such schemes might be carried out by one of these methods: (1) an excess of the hydrocarbon mixture might be added to solid antimony chloride and the one complexed less by the halide separated by filtration, (2) equal moles of hydrocarbon mixture and antimony chloride might be added and the less stable complex decomposed thermally, (3) the complexes might be formed in an inert solvent and the less stable one separated by extraction, distillation, etc. These are only suggestions; other methods could be devised. Kinetic factors must be considered also. No measure of the time required for the complexes to form was made in this work, although it is not likely to be much different for these systems.

The thermodynamic stability of these complexes is properly measured by the standard free energy change in their dissociation, ΔF^o. Values of ΔF^o have been computed and tabulated in Table VIII, along with the related values for ΔH in this temperature range.

Table VIII

Thermocynamic Constants for Complexes

Complex	K_p	ΔF^o_{298}, kcal./mole	ΔH, kcal./mole
$2SbCl_3 \cdot C_6H_6$	7.1	-2.77	12.6
$2SbCl_3 \cdot C_6H_5CH_3$	6.5	-2.82	7.2
$2SbCl_3 \cdot C_6H_5C_2H_5$	5.1	-2.96	9.6
$2SbCl_3 \cdot \underline{m}\text{-}C_6H_4(CH_3)_2$	2.8	-3.32	9.5

All values of ΔF^o being negative, the complexes are thermodynamically stable with respect to the separate reagents. The order of values is what would be expected from the known basicities of the hydrocarbons (2). Whether the small difference in K_p for ethylbenzene and m-xylene is enough to justify more detailed study by one of the methods outlined above is uncertain. Also it is not known what the equilibrium constants are at various concentrations in an inert solvent such as pentane.

Heats of dissociation of the complexes are not greatly different; the most puzzling is the low value for toluene. The relatively high one for benzene may be associated with the symmetry of benzene and its consequently better fit in the crystal lattice.

Experimental difficulties were encountered to some degree in making measurements on the toluene system and to a much larger degree on the ethylbenzene and m-xylene systems. These were caused by: (1) relatively low volatility of the hydrocarbons (especially from a saturated solution of $SbCl_3$) at room temperature, (2) the low melting points of the complexes (see Table II), which prevented measurements on the solids above 35°, and (3) the long time required for the systems to come to equilibrium after an evacuation. To aid in sweeping foreign gases from the system, a smaller (10-ml.) flask was used for A (see Fig. 6); it was then possible to purify the complex with use of very little excess hydrocarbon.

The molecular ratios in the complexes are evidently

$$2SbCl_3 \cdot ArH$$

Values for the benzene and toluene complexes are slightly high because it is impossible not to overrun the dissociation plateau a little. This 2:1 ratio agrees with the phase rule data given in Table II. Values for ethylbenzene and m-xylene were not determined, primarily because of the extremely long time required for these systems to reach equilibrium. It was therefore virtually impossible to tell when the dissociation plateau was reached.

Measurements were made above the melting point on the toluene complex (Fig. 8). The curve for the liquid complex is rather surprising as one would expect it to have a smaller negative slope and hence to signify a smaller heat of dissociation than for the solid. The results are explicable on a phase rule basis. For the solid complex system there are 3 phases ($SbCl_3$, $SbCl_3 \cdot 0.5$ toluene, and toluene vapor) and 2 components. Application of the phase rule gives one degree of freedom:

$$F = C - P + 2 = 2 - 3 + 2 = 1$$

and only the temperature need be fixed to define the system. For the liquid complex only 2 phases are present; $SbCl_3$ dissolved in liquid complex and toluene vapor. This gives a degrees of freedom:

$$F = C - P + 2 = 2 - 2 + 2 = 2$$

Therefore both temperature and composition of liquid phase are needed to define the system and what was measured, of course, was not the vapor pressure of the pure complex.

Specific recommendations for further experimental study to devise a separation method based on complex formation are outlined below. Both would depend on the assumption that $SbCl_3$ would selectively complex with m-xylene in a mixture of m-xylene and ethylbenzene or in a mixture of these hydrocarbons and an inert solvent.

(1) Various known mole ratios of ethylbenzene and m-xylene are heated with antimony chloride, the hydrocarbon-antimony chloride ratio being greater than one. After cooling, the crystals of the complex are filtered off and the filtrate analyzed to determine if any selectivity is evidenced in the complex formation.

(2) Various known mole ratios of m-xylene and ethylbenzene in an inert solvent (possibly pentane would serve) are heated with $SbCl_3$. Different mole ratios of aromatic hydrocarbon to $SbCl_3$ would need to be tried but probably an excess of aromatic hydrocarbon is best at first. Then, assuming that one hydrocarbon were selectively complexed, methods such as the following might serve to remove the complex from the mixture. (2) At low solvent-solute ratios crystallization methods may be employed, (b) extraction of the complex (or possibly the aromatic compound remaining free in the solution) with some hydrocarbon-insoluble liquid may be tried, (c) distillation at atmospheric or reduced pressure might also serve to effect a separation.

SUMMARY

Two methods have been investigated for possible use in the commercial separation of m-xylene and ethylbenzene. They are: (1) extractive distillation and (2) selective solid complex formation.

Approximately fifty organic compounds, representing the major classes of compounds in this field, and seven inorganic compounds, all metallic halides, were surveyed as possible extractive distillation solvents. The boiling point method of Weissberger (123) was used. This permitted survey of a relatively large number of compounds for possible use as extractive solvents. None of the organic compounds showed any promise as extractive solvents by the experimental method employed. Among the inorganic compounds, only antimony chloride, where employed at reduced pressures and high antimony chloride / hydrocarbon ratios, showed much promise for this purpose. The application of antimony chloride as solvent, however, has already been patented. The reason for its apparently anomalous behavior is not apparent, but it is possibly due to the unique Lewis acid properties of the chloride.

In studying complex formation for possible use in this separation, some basic studies of the properties of the antimony chloride - aromatic hydrocarbon complexes were made. Measurement of the dissociation constants (vapor pressures) of the pure complexes of antimony chloride

with each of the hydrocarbons benzene, toluene, ethylbenzene, and m-xylene were made over rather short temperature ranges around room temperature. This temperature range was limited by the low melting points of all of the complexes except that of benzene. From these data the free energies of formation and heats of dissociation of each of the complexes were calculated. Heats of dissociation for the m-xylene and ethylbenzene complexes are almost identical. The order of stabilities of the complexes as seen from the dissociation constants and expressed in terms of the hydrocarbon concerned, is m-xylene > ethylbenzene > toluene > benzene. This is to be expected from the known basicities of the hydrocarbons. The equilibrium constants and hence the free energy changes for the reaction

$$2SbCl_3 \cdot ArH \rightleftharpoons 2SbCl_3 + ArH$$

for the m-xylene- and ethylbenzene-antimony chloride complexes are different enough to warrant some further experimental work. This has been outlined in the discussion of experimental results.

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THESIS TITLE: THE SEPARATION OF ETHYLBENZENE AND m-XYLENE

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