LIQUID-VAPOR EQUILIBRIA
IN THE SYSTEM:
ISOPROPYL ALCOHOL-DIBROMOMETHANE

by

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INTRODUCTION

An azeotropic mixture is defined as a system which, at constant pressure, boils or distills without change in composition and which generally has a higher or lower boiling point than any of its components.

In recent years, Lecat and others have worked with many binary and ternary systems to determine which ones form azeotropes. Horsley has made several collections of data available (5, 6, 7,). The latter reference includes some 14,000 systems. Unfortunately, information on many of these mixtures is incomplete and the azeotrope is described as being above or below a certain boiling point and composition.

The purpose of this research project was to determine more closely the liquid vapor equilibrium curve and the boiling point and composition of the azeotrope formed in the system isopropyl alcohol -- dibromomethane. This system is reported in Horsley's book (7) from Lecat (10) as forming an azeotrope at a boiling point less than 81.0°C. and with a composition greater than 32 weight percent dibromomethane. Both components have boiling points of less than 100°C. and their refractive indices are well separated, thus making investigation with fairly simple, but accurate apparatus possible (8).

HISTORICAL

Liebig was probably the first (4) to observe and report on an azeotropic mixture. In the year 1832, he was working with ethylene dichloride and water and discovered that a mixture of these compounds boiled lower than either pure substance (11). Dalton, in the same year, observed the first maximum boiling azeotrope -- HCl and water. This was found to have such a constant boiling point and composition that it has been used for many years as a standard acid in quantitative determinations. Berthelot was one of the first to observe a homogeneous (single phase) minimum boiling azeotrope -- ethanol and carbon disulfide. His work was done in 1863. He also noted that "in a mixture the liquids do not always distill in order of decreasing volatility."

Only a small number of constant boiling mixtures were discovered in the 19th century. Most of these were explained as compound formation between the two components. Ostwald suggested the use of the term "hylotropic" (from the Greek hylos meaning substance and tropos meaning changing) (12) for these mixtures. Sir Henry Roscoe demonstrated in 1861 that a constant boiling mixture was not a molecular compound and that its composition varied with pressure.

After the turn of the century, extensive research was done by Sydney Young and Maurice Lecat. Young, in 1902, discovered the first ternary azeotrope, a minimum boiling mixture of ethanol, benzene and water. This system soon became important in the manufacture of absolute alcohol. Lecat has probably contributed most to the literature of azeotropy with his study of several thousand mixture and the determination of constant boiling mixtures for many of them. One of the mixtures he worked with was isopropyl alcohol and dibromomethane (10).

The formation of an azeotrope is a sign of non-ideality of the mixture. Present theory attributes azeotropism mainly to the effects of hydrogen bonds. Hydrogen can form a coordinate bond between two molecules containing oxygen, nitrogen, or fluorine, or between one of these atoms and carbon. Some of these bonds are quite strong, others are relatively weak. The deviation from ideality of a system depends upon the strength of hydrogen bonds formed by the components.

Actual formation of an azeotrope depends upon the magnitude of deviation from ideality and the difference in boiling point of the two pure components. The smaller the deviation, the smaller the difference in boiling point must be before azeotrope formation. A positive deviation from Raoult's Law will form a minimum boiling mixture under proper conditions, while a negative deviation will produce a maximum boiling mixture. It is interesting to note that minimum boiling azeotropes are much more common than maximum boiling mixtures (1).

APPARATUS

The major pieces of apparatus used in carrying out this research were a Cottrell-Choppin Liquid-Vapor Equilibrium Apparatus and an Abbe Refractometer.

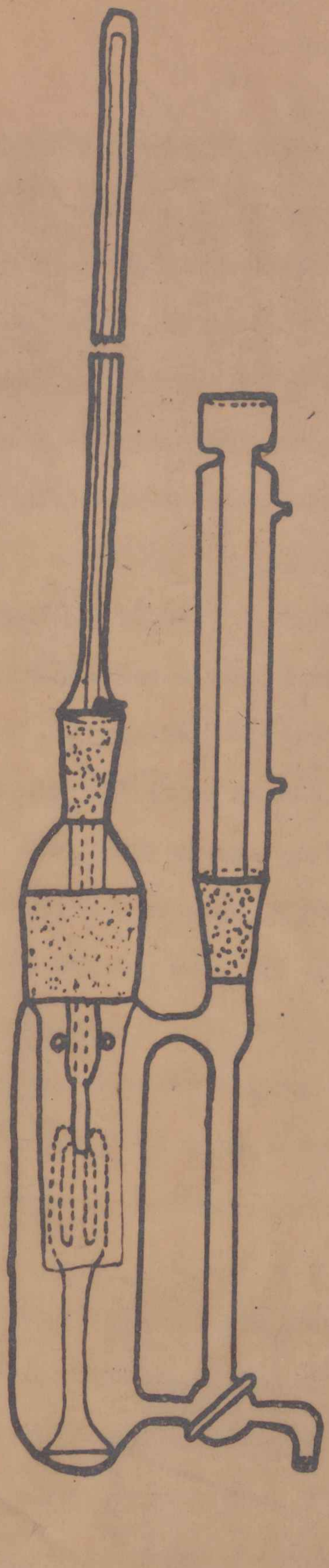
Cottrell-Choppin Apparatus (14):

This apparatus is a combination of the familiar Cottrell pump and a modified Cottrell molecular weight apparatus. (See Fig. 1). The modification is made by the addition of a three-way (T-type) stopcock so that in one position the liquid can reflux; in another, a sample may be withdrawn from the side arm (vapor); and in the third position, the bottom of the flask (liquid) may be tapped. A thermometer accurate to 0.1°C. is used for this work. This piece of apparatus is manufactured by E. H. Sargent & Co.

Advantages of using this apparatus are: It is simply constructed and easy to operate. It comes to equilibrium quickly and yields quite accurate data. It has the advantage of not being complicated and costly, while retaining much of the precision of the better apparatus (13). Similarly, it is more accurate than the very simple apparatus used in most physical chemistry experiments (9).

Abbe Refractometer:

Refractive indices provide a simple and accurate way to determine composition. An Abbe refractometer manufactured by the Bausch and Lomb Optical Company was used. A refractometer is a common enough piece of laboratory apparatus that it is not felt necessary to describe it in full here. Many good descriptions can be found in the literature (2).



COTTRELL CHOPIN EQUILIBRIA APPARATUS

FIG. I

EXPERIMENTAL PROCEDURE

The well known system ethyl alcohol -- water was used to develop techniques of operation. An attempt was made to remove traces of water from absolute ethanol according to the method described by Fieser (3). This apparently was unsuccessful, or all removable water was gone, as the refractive index was exactly the same both before and after the procedure was carried out.

Basically, to establish curves, a binary mixture of any composition is brought to equilibrium and samples of the liquid and vapor are analysed. A charge of about 100 ml. of the mixture is placed in the apparatus and refluxed vigorously until an equilibrium is reached (3 to 10 minutes) as noted by a constant temperature. The first charge used was 100 ml. of either pure substance. The following charges were made by adding some (about 5 ml.) of the second component and then filling to about 100 with mixture drawn off in the preceding sampling procedure.

The boiling point vs. refractive index curve obtained with ethyl alcohol and water was quite similar to known curves. Since this part of the experiment was carried out only to perfect techniques, it was not felt necessary to carry it to completion.

Purity of the Eastman Dibromomethan and Eastman Isopropyl Alcohol (both "White Label") was checked with a Perkin-Elmer Vapor Fractometer Model 154. A two meter "A" column (diisodecyl phthalate liquid phase) was used at 80°C. The carrier gas was helium at 17 pounds pressure. The curves for both compounds showed them to be almost completely free from impurities. It was estimated that each was at least 99.9% pure.

Mixtures of isopropyl alcohol and dibromomethanewere brought to equilibrium and tested as described above. The starting substance was pure isopropyl alcohol with dibromomethane being added in 5 ml. batches. When a fairly constant boiling point was reached, and when a similar composition of liquid and vapor was indicated by proximity, and on addition of another 5 ml., reversal of refractive indices, the apparatus was drained. This mixture was saved for further analysis later.

The above procedure was again carried out using pure dibromomethane at the start and adding isopropyl alcohol. In this part of the experiment, some difficulty was encountered in that on boiling, the Cottrell pump had a tendency to be lifted on the bubbles until it hit the thermometer and lost its effectiveness. This was thought to be due to the density of the mixture and the vigor of the boil. It was controlled by the use of a burner hood to concentrate the heat, and careful control of the size and position of the flame under the flask.

When the proximity and subsequent reversal of refractive indices again indicated the peak of the curve, the flask was emptied and the mixture added to the one from the previous part of the experimentation. They were placed in a distilling flask and boiled off. Since isopropyl alcohol and dibromomethane form a low boiling azeotrope, the major fraction boiled off first. The temperature was not completely constant, but ranged from 78.40 to 78.70 (uncorrected). Refractive indices were taken for every 0.1 degree rise. These showed that the composition rose proportionally to the temperature from 0.680 to 0.685 mole fraction isopropyl alcohol. This data is shown in Table 4. About 140 ml. out of 200 boiled over between these two points.

A standard composition curve was prepared by making up mixtures of known composition and taking their refractive indices. This data can be found in Table 1. The resulting curve of refractive index vs. composition is shown in Fig. 2.

From the standard curve, the compositions of equilibrium samples can be determined. Figure 3 shows the plot of both liquid and vapor composition against boiling point. The plot of liquid composition vs. vapor composition is shown in Fig. 4. The boiling points used are uncorrected as dp/dt data for the various mixtures are not available. The boiling points were recorded under pressures ranging from 749 to 761 mm. of Hg. With this factor in mind, Fig. 4 would be considered to represent a curve of higher validity than Fig. 3.

TABLE 2

EQUILIBRIUM DATA

starting with pure isopropyl alcohol

	Vapor		Liquid	
B. P. °C.	n_D^{25}	N Iso	n_D^{25}	N Iso
81.99	1.3747	1.000	1.3748(a)	1.000
81.00	1.3872	0.899	1.3820	0.940
80.10	1.3962	0.839	1.3882	0.891
79.51	1.4061	0.783	1.3956	0.844
78.98	1.4079	0.768	1.4022	0.800
78.90	1.4126	0.740	1.4080	0.767
78.69	1.4162	0.719	1.4130	0.738
78.70	1.4212*	0.685	1.4209*	0.687
78.69	1.4222*	0.679	1.4252*	0.659

(a) - Literature value -n_D^{25} -- 1.3748 to 1.3754.

* Note reversal of refractive index and composition.

TABLE 3

starting with pure dibromomethane

	Vapor		Liquid	
B. P. °C.	n_D^{25}	N_{Iso}	n_D^{25}	N_{Iso}
96.5	1.5345	0.000	1.5344(b)	0.000
91.02	1.4860	0.278	1.5298	0.040
87.30	1.4672	0.390	1.5219	0.080
84.95	1.4740	0.350	1.5147	0.120
83.51	1.4542	0.470	1.5071	0.161
82.30	1.4471	0.516	1.5007	0.200
81.50	1.4411	0.554	1.4940	0.232
80.80	1.4382	0.572	1.4878	0.268
80.39	1.4372	0.579	1.4816	0.304
80.01	1.4390	0.569	1.4760	0.388
79.69	1.4352	0.592	1.4708	0.369
79.19	1.4363	0.586	1.4658	0.401
78.90	1.4340	0.600	1.4611	0.429
78.73	1.4304	0.625	1.4561	0.459
78.76	1.4321	0.612	1.4519	0.486
78.61	1.4292	0.630	1.4480	0.510
78.60	1.4284	0.637	1.4439	0.538
78.50	1.4288	0.633	1.4402	0.560
78.41	1.4265	0.650	1.4368	0.582
78.38	1.4256	0.656	1.4338	0.602
78.29	1.4228	0.676	1.4303	0.623
78.25	1.4248	0.660	1.4275	0.644
78.21	1.4221	0.679	1.4250	0.660
78.18	1.4212*	0.684	1.4222*	0.678
78.05	1.4219*	0.680	1.4198*	0.695

(b) Literature value not given at 25°C.

n_D^{20} -- 1.5419

* Note reversal of refractive index and composition.

TABLE 4

Azeotropic distillation

B. P. °C.	n_D^{25}	Vapor N Iso
78.40	1.4235	0.680
78.50	1.4232	0.682
78.60	1.4229	0.684
78.70	1.4228	0.685

SUMMARY

Lecat states that the system isopropyl alcohol -- dibromomethane forms an azeotrope (constant boiling mixture) with a boiling point of less than 81.0°C. and a composition of greater than 32 wt. percent dibromomethane. Experimentation using a Cottrell-Choppin Vapor-Liquid Equilibrium Apparatus and an Abbe Refractometer has shown the boiling point to be 78.4 -- 78.7°C. and the composition to be 0.680 -- 0.685 mol fraction isopropyl alcohol (approximately 57.65 wt.% dibromomethane).

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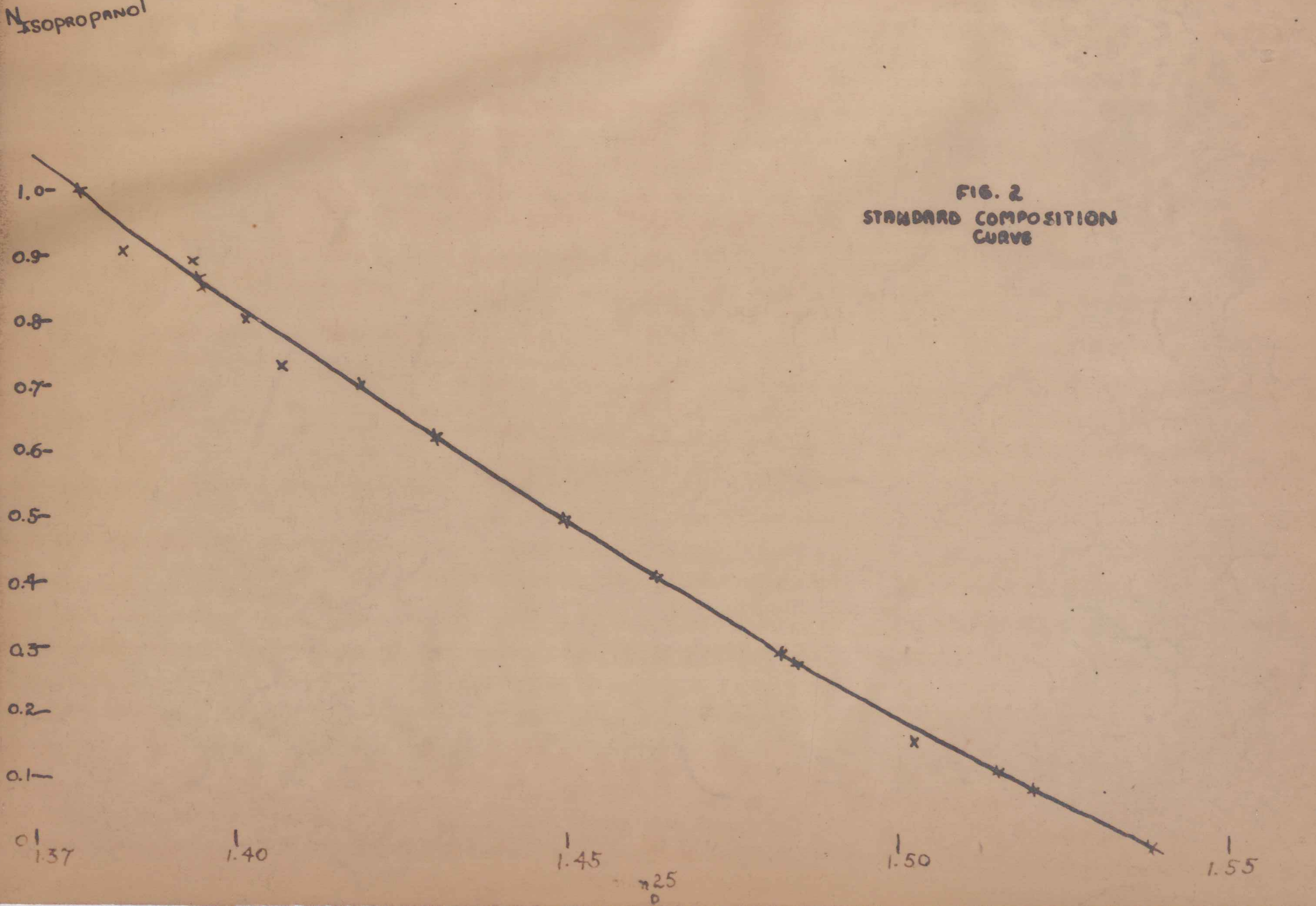

FIG. 2
STANDARD COMPOSITION
CURVE

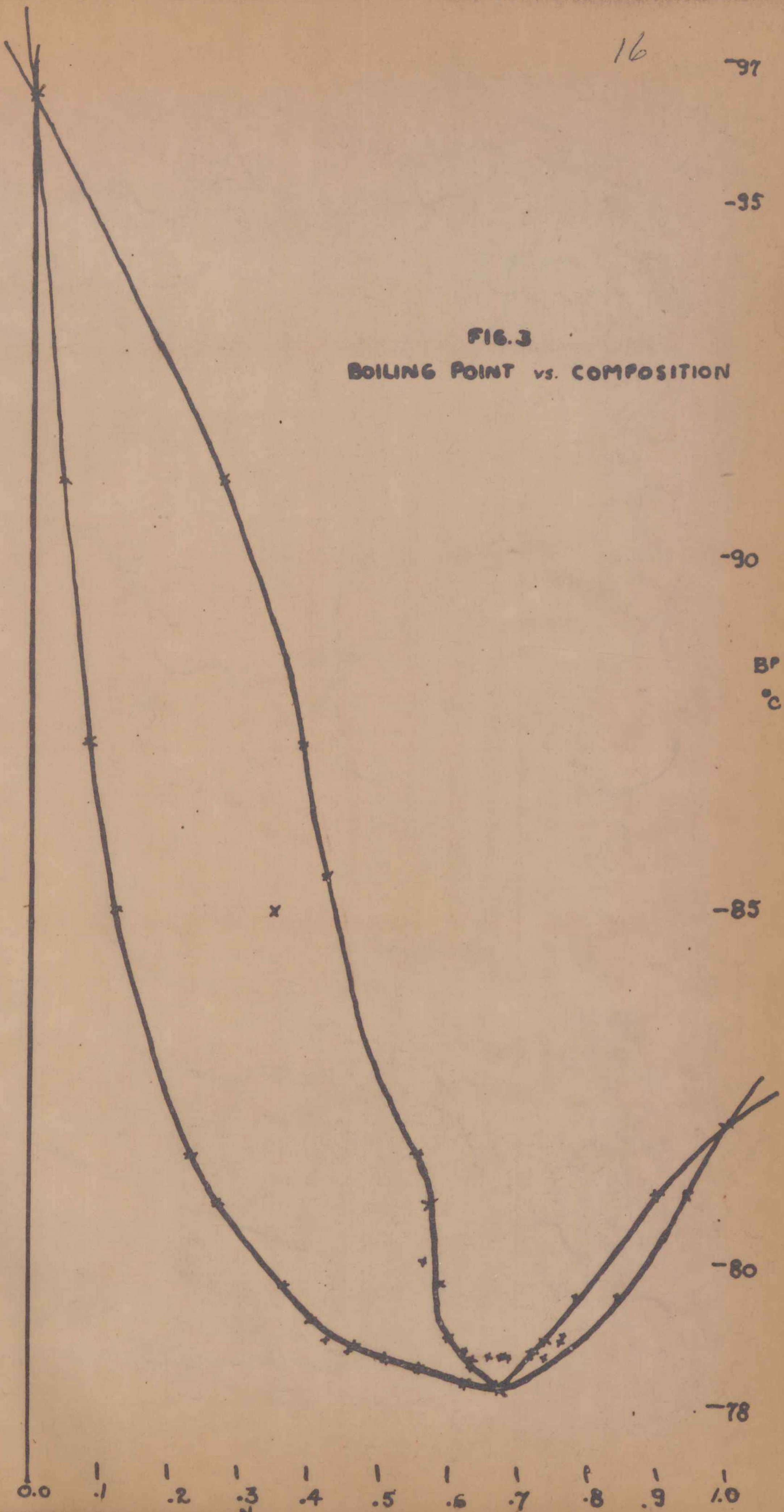

FIG. 3
BOILING POINT vs. COMPOSITION

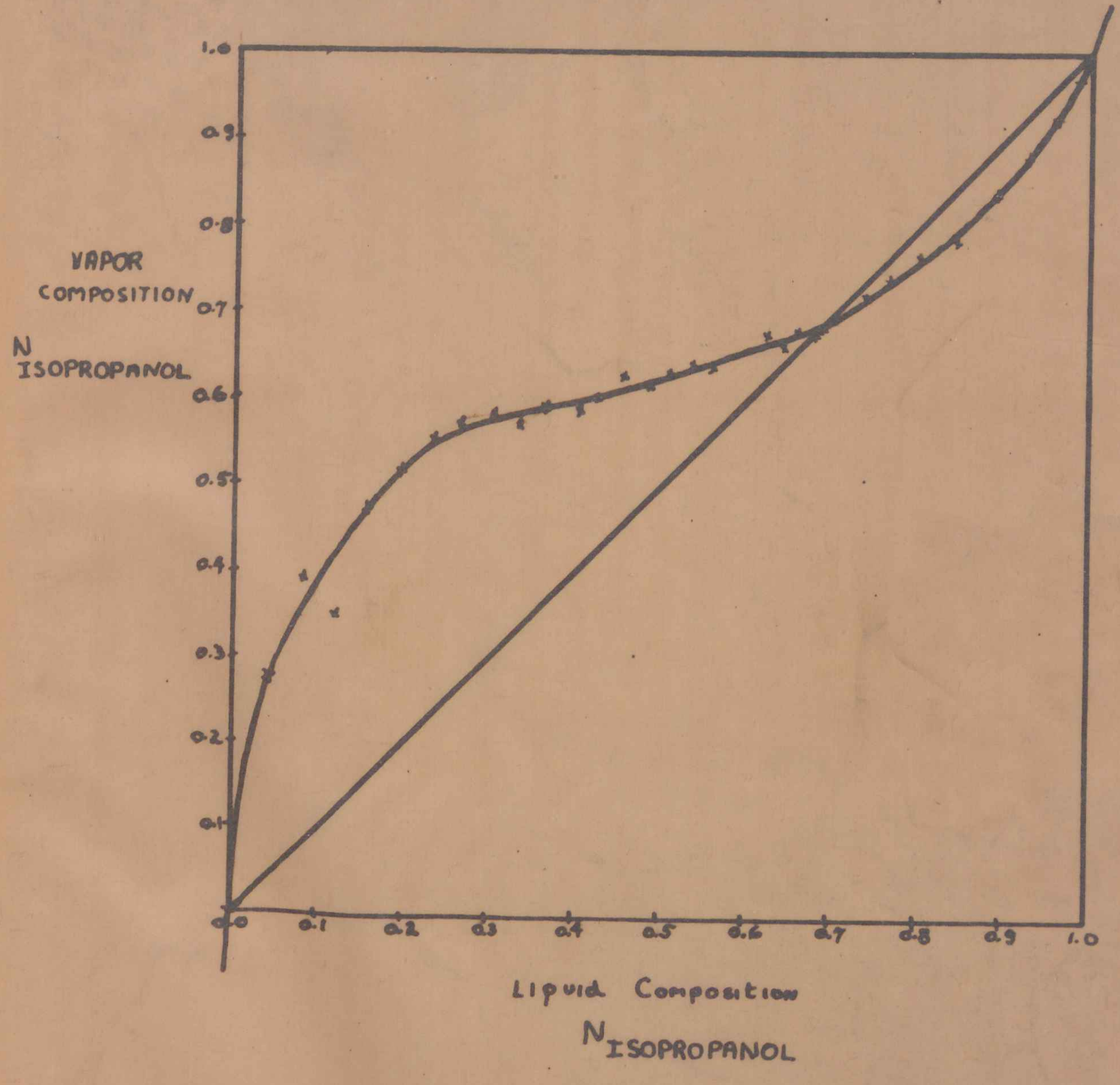

FIG. 4
LIQUID COMPOSITION
vs
VAPOR COMPOSITION