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Viscosity of a three component system, acetone-ethanol-water, at 25°C and 30°C

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VISCOSITY OF A THREE COMPONENT SYSTEM
ACETONE-ETHANOL-WATER, AT 25°C AND 30°C

BY

PETER F. WIDMER

A THESIS
SUBMITTED TO THE FACULTY OF
THE DEPARTMENT OF CHEMICAL ENGINEERING
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ABSTRACT

The viscosity in the three component system Acetone-Ethanol-Water has been determined over a range of compositions at two different temperatures, 25°C and 30°C. Compositions have been varied in increments of ten percent by weight to cover all possible combinations of the three components. The data obtained are presented on triangular coordinate graph paper with lines of constant viscosity indicated and also in tabular form.

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INTRODUCTION

All liquids exhibit a resistance to flow. This property which opposes the relative motion of adjacent portions of the liquid is known as viscosity.

When a liquid flows it is probable that the layer of liquid in contact with the walls next to which it is flowing is stationary. The effect of the viscosity of the liquid will slow down the next layer and that layer the next and so on with a diminishing extent into the body of the liquid. J. L. M. Poiseuille used this theory to determine the coefficient of viscosity, V , of a liquid flowing through a narrow tube of radius r cm. and l cm. in length under a pressure of P dynes/square cm. flowing at a uniform velocity of v ml. in t secs. The relationship he determined was

$$V = \frac{\pi Pr^4 t}{8vl} .$$

G. G. Stokes made virtually the same assumptions in determining the viscosity of a liquid by having a small sphere fall through the liquid. Here it is believed that the thin layer of liquid in immediate contact with the sphere is virtually at rest and this layer of liquid has a slowing effect on the subsequent layer etc. The relationship determined by Stokes for a sphere of radius r , density d falling through a liquid of density d' with a viscosity V and having a velocity v where g represents the force of gravity is

$$\nu = \frac{2gr^2(d-d')}{9V}$$

The effect of an increase in temperature upon the viscosity of a liquid is to decrease its value. Several equations connecting viscosity and temperature have been set forth but those of the exponential type as derived by S. Arrhenius are preferred. This type of equation is written

$$V = Ae^{B/RT}$$

where A and B are constants for the given liquid, R the gas constant, T the temperature and V the viscosity of the liquid.

It has been surmised that the viscosity of a liquid mixture could be determined through the use of simple theoretical equations. E. C. Bingham advanced the relationship

$$F = x_a F_a + x_b F_b$$

where F represents the fluidity, which is the reciprocal of the viscosity, of the mixture and F_a and F_b the values for the fluidity of the pure components whose mole fractions in the mixture are x_a and x_b . J. Kendall proposed a more satisfactory relationship expressed by

$$\log F = x_a \log F_a + x_b \log F_b .$$

Mixtures of similar liquids behave ideally and obey this

equation. If the components of the mixture have a tendency to form complexes in the liquid state the observed fluidities are less than the calculated values and therefore, there is an increase in viscosity upon mixing. Water and ethanol and water and acetone exhibit this type of behavior.

A number of binary systems have been investigated and data on these systems may be found in the International Critical Tables. A literature search failed to disclose any data on the viscosity of the ternary system acetone, ethanol, water. However, it is known that in the binary systems of ethanol-water and acetone-water as the concentrations of ethanol and acetone are increased the viscosity of the resulting mixtures increases to a maximum value and then decreases again. This behavior posed the question as to what effect these binary systems would have upon each other if the three different components making up the two binary systems were combined into one ternary system. Since these are not similar liquids and their mixtures do not behave ideally, the viscosity of this system cannot be predicted by any formula such as that of Bingham or of Kendall and must be determined experimentally.

The present investigation was undertaken to determine the effect of varying the individual components of the ternary system, acetone-ethanol-water, upon the viscosity of the mixture. The range is covered at increments of ten

percent by weight at both 25°C and 30°C. The 25°C temperature was selected because there are several sets of published data of viscosity of binary systems at this temperature. In order to observe the effect of temperature on the viscosities of the mixtures in this system, data were also obtained at a second temperature. The second temperature of 30°C was selected since at temperatures over 30°C serious losses due to evaporation occur. The data obtained are presented on triangular coordinate graph paper with lines of constant viscosity indicated and also in tabular form.

Viscosity values for the three binary systems, acetone-water, ethanol-water and acetone-ethanol, which are contained within this ternary system, are available in the International Critical Tables (1). With the available data a tabular and also a graphic comparison of literature and experimental values are presented.

THE MATERIALS

The dry ethanol used for the acetone-ethanol system and for the determination of the viscosity of ethanol was prepared by using the method described by Weissberger (2). Absolute ethanol was placed in a flask containing drierite and shaken for a period of 24 hours. The ethanol was then gently distilled from the flask to separate it from the drierite. The temperature was controlled to maintain a vapor temperature of 78°C to 78.5°C . The first and final increments of distillate were discarded in an effort to secure a pure product. It was found necessary to repeat this procedure three times to secure a final product containing a maximum water content of 0.06%.

A similar procedure was described by Weissberger (3) and was used to obtain an essentially dry sample of acetone. In this instance the vapor temperature of the distillate was maintained at 56°C to 56.5°C . It was found after the second attempt that a product with a water content of 0.03% was obtained.

All other samples were prepared from USP ethanol which assayed 92.3% ethanol by weight and from chemically pure acetone which was found to contain 99.5% anhydrous acetone by weight upon assay.

Freshly distilled water made in the laboratory was used

in preparing the necessary samples.

THE EQUIPMENT

A torsion balance having a sensitivity of 2 milligrams was used to make up all samples. All samples prepared were fifty grams in weight which gave the weighings an accuracy of 4 parts in 100,000. The samples were weighed directly into 100 milliliter glass stoppered flasks which were immediately stoppered and in the case of the anhydrous samples wax-sealed to exclude the possibility of atmospheric moisture contaminating the samples. All samples were stored at 4°C to minimize the possibility of losses due to evaporation.

The viscosities were determined by using Ostwald-Fenske tubes. The viscometer sizes used were #100 and for more fluid samples #50. The calibration constant for the #100 tube was found to be 0.02664 at 25°C and 0.02675 at 30°C. The calibration constant for the #50 tube was 0.0033514 at 25°C and 0.003379 at 30°C.

The timer used in the viscosity determinations was a Waltham stopwatch with a sixty second dial and 0.1 second divisions accurate to 0.1 second.

A ten milliliter pycnometer was used to determine the density of the samples. All density weighings were made to 0.1 milligram on an analytical balance having a sensitivity of 1/20 milligram.

A ten liter battery jar fitted with an immersion heater and a mixer was used for the constant temperature bath. The temperature of the bath was maintained $\pm 0.1^{\circ}\text{C}$ by means of a variac control and checked with a standard thermometer graduated in 0.1°C divisions.

THE METHOD

Density Measurements

The samples whose density was to be measured were stored at 4°C thus insuring that the samples were below the desired temperature of 25°C or 30°C. The samples were placed in the ten milliliter pycnometer and the cap which holds a self-contained thermometer was placed on the pycnometer. The liquid was warmed by placing it in a constant temperature bath of 25°C or 30°C as desired. As the sample was warmed its volume expanded and the excess flowed from the side arm capillary. This excess was cleaned off with a cellulose wipe as it appeared. At the proper temperature the side arm cap was placed on the pycnometer and the sample weighed on an analytical balance. The pycnometer was standardized for volume, since the density of the solutions is required to determine the viscosity, by using freshly distilled water as the sample. Then by dividing the weight of the sample by the published values for the absolute densities of water at 25°C and 30°C, as the case required, an accurate calculation of the volume of the pycnometer was made possible.

Viscosity Measurement

The procedure followed in the measurement of the viscosity of the samples was that described in the ASTM (4). The instrument is filled by holding it in an inverted

position with the end of the capillary immersed in the sample. Vacuum is then applied to the other arm of the viscometer and sample drawn into it until it reaches the etched mark of the working capillary. This insures a constant volume of liquid in the viscometer. The instrument is then placed in an upright position and the excess sample wiped off the capillary arm with a cellulose wipe. It is then placed into a constant temperature bath in a vertical position, so that the upper bulb is below the surface of the bath liquid, for a period of not less than ten minutes to allow the sample to attain the proper temperature. After the desired temperature has been attained vacuum is applied to the capillary arm and the sample drawn up to a point approximately 5 mm. above the etched mark between the bulbs. The vacuum is then released and the time for the meniscus to pass from the upper to the lower mark is measured and recorded. This process is repeated until at least three consistent times are obtained and the average value of these three times is used to calculate the viscosity.

The viscometer tubes were standardized by using freshly distilled water as the sample to be measured. Then using the literature value for the viscosity it is possible to calculate the calibration constants for both instruments used at both 25°C and 30°C.

In the viscosity determinations of the anhydrous samples it was necessary to make a modification to the procedure as previously outlined. After filling the viscometer a drying tube filled with fresh silica gel was attached to the open end of the viscometer to reduce the possibility of the samples taking on moisture from the atmosphere. The instrument was then placed in the constant temperature bath and the procedure as previously described was followed.

DISCUSSION

Binary Systems

An examination of the data obtained for the binary system of ethanol-water at both 25°C and 30°C which is listed in Table #1 and also presented graphically in Figures #1 and #2, indicates that as the concentration of alcohol is increased the viscosity of the system increases to a maximum, at the composition of 45% ethanol, 65% water, and then as the concentration of alcohol is further increased the viscosity decreases. A comparison of the experimentally determined values with those published in the International Critical Tables (1) is presented. The experimental values are in good agreement with the published values which indicates that the technique, equipment and method used in determining these values is valid.

The data obtained for the binary system of acetone-water also indicate that as the concentration of acetone is increased, the viscosity of the system increases to a maximum at approximately 34% acetone, 66% water and then as the acetone concentration is further increased the viscosity falls. This was found to be the case at both 25°C and 30°C as indicated in Table #1 and Figures #3 and #4. Here again a comparison with the published values of viscosity for this system at 25°C as found in the International Critical Tables (1) shows good agreement with the

experimentally determined values.

The binary system of acetone-ethanol decreased in viscosity as the concentration of acetone in the system was increased at both 25°C and 30°C. These data are set forth in Table #1 and Figures #5 and #6. The comparison of the experimentally determined viscosity with that published in the literature (1) for the system at 25°C once again indicates a very close agreement of experimental values with published values.

Ternary System

An examination of the complete viscosity data for the ternary system, which is most clearly shown in Figures #7 and #8, and also presented completely in Tables #1 and #2, indicates that the characteristic rise in viscosity of the mixtures to a maximum value and then falling off again as first seen in the binary system of ethanol-water is carried over into the ternary system as the amount of acetone is increased up to and including 30% acetone. At and above concentrations of 40% acetone the viscosity of the systems, when holding the concentration of acetone constant, merely decreases as the concentration of alcohol is increased. The maximum value of viscosity for the systems containing from 0% to 30% acetone appears to fall between concentrations of 50% to 60% water. This is characteristic of the system at both 25°C and 30°C.

The characteristic behavior of the binary system acetone-water reaching a maximum viscosity and then decreasing as the acetone concentration is further increased is also noted in the ternary system, acetone-ethanol-water, in mixtures up to those containing approximately 20% ethanol. As the ethanol concentration is increased to 30% and higher this maximum is no longer evident and the viscosity merely falls as the concentration of acetone is increased. This phenomenon is exhibited both at 25°C and 30°C. In both cases the maximum is reached when the concentration of water in the system is between 60% and 70%.

The binary system of acetone-ethanol in which the viscosity decreases as the concentration of acetone is increased continues to follow this trend throughout the ternary system. When the water in the samples is held constant and the other materials varied it is found that the viscosity of the samples decreases as the amount of acetone in the system is increased.

To aid in reading and correlating the plot of viscosity values in Figures #7 and #8, lines of constant viscosity at 4, 8, 12, 16, and 20 millipoise were determined and drawn on the plot.

The temperature effect was found to vary with the composition in a manner which defied simple correlation.

Therefore, it is presented without further treatment.

TABLE I

VISCOSITY OF BINARY SYSTEMS

% ethanol	% acetone	% water	Viscosity at 25°C		Viscosity at 30°C	
			Determined	Published	Determined	Published
0	0	100	-	8.937	-	8.007
10	0	90	13.17	13.2	11.58	11.53
20	0	80	18.14	18.0	15.32	15.3
30	0	70	21.94	22.0	18.41	18.4
40	0	60	23.61	23.7	19.76	19.9
50	0	50	23.54	23.6	19.89	20.0
60	0	40	22.32	22.3	19.00	19.0
70	0	30	20.08	20.2	17.33	17.4
80	0	20	17.24	17.3	15.08	15.1
90	0	10	14.26	14.2	12.77	12.7
100	0	0	10.96	11.01	10.05	9.97
0	10	90	10.91	10.87	10.02	-
0	20	80	12.78	12.75	11.50	-
0	30	70	13.54	13.58	12.56	-
0	40	60	13.49	13.51	12.41	-
0	50	50	12.36	12.40	11.29	-
0	60	40	10.59	10.40	9.45	-
0	70	30	8.23	8.25	7.51	-
0	80	20	6.10	6.13	5.30	-
0	90	10	4.36	4.35	3.50	-
0	100	0	3.15	3.17	2.50	-

TABLE I

% ethanol	% acetone	% water	Viscosity at 25°C millipoise		Viscosity at 30°C millipoise	
			Determined	Published	Determined	Published
10	90	0	3.37	3.34	2.70	-
20	80	0	3.56	3.55	2.95	-
30	70	0	3.86	3.85	3.20	-
40	60	0	4.23	4.27	3.60	-
50	50	0	4.74	4.77	4.10	-
60	40	0	5.40	5.40	4.59	-
70	30	0	6.36	6.33	5.81	-
80	20	0	7.44	7.48	6.87	-
90	10	0	9.08	9.12	8.39	-

TABLE IIVISCOSITY OF TERNARY SYSTEM

% ethanol	% acetone	% water	Viscosity at 25°C millipoise	Viscosity at 30°C millipoise
10	10	10	15.32	13.09
20	10	70	18.51	15.94
30	10	60	20.20	17.57
40	10	50	20.39	17.52
50	10	40	18.90	16.75
60	10	30	17.34	15.24
70	10	20	14.91	13.14
80	10	10	12.63	10.85
10	20	70	15.85	13.58
20	20	60	17.98	15.05
30	20	50	18.12	15.23
40	20	40	17.46	14.73
50	20	30	15.35	13.43
60	20	20	12.98	11.64
70	20	10	10.37	9.31
10	30	60	15.84	13.34
20	30	60	15.93	13.73
30	30	40	15.10	13.16
40	30	30	13.55	11.90
50	30	20	11.51	10.32
60	30	10	9.63	8.26
10	40	50	14.17	12.32

TABLE II

% ethanol	% acetone	% water	Viscosity at 25°C millipoise	Viscosity at 30°C millipoise
20	40	40	13.38	11.67
30	40	30	11.85	10.59
40	40	20	9.96	9.11
50	40	10	7.74	7.04
10	50	40	11.89	10.57
20	50	30	10.52	9.38
30	50	20	8.73	8.05
40	50	10	6.90	6.49
10	60	30	9.42	8.59
20	60	20	7.88	7.35
30	60	10	6.24	5.83
10	70	20	7.17	6.65
20	70	10	5.71	5.21
10	80	10	5.27	4.60

Figure 1
Viscosity of Ethanol-Water solution at 25° C

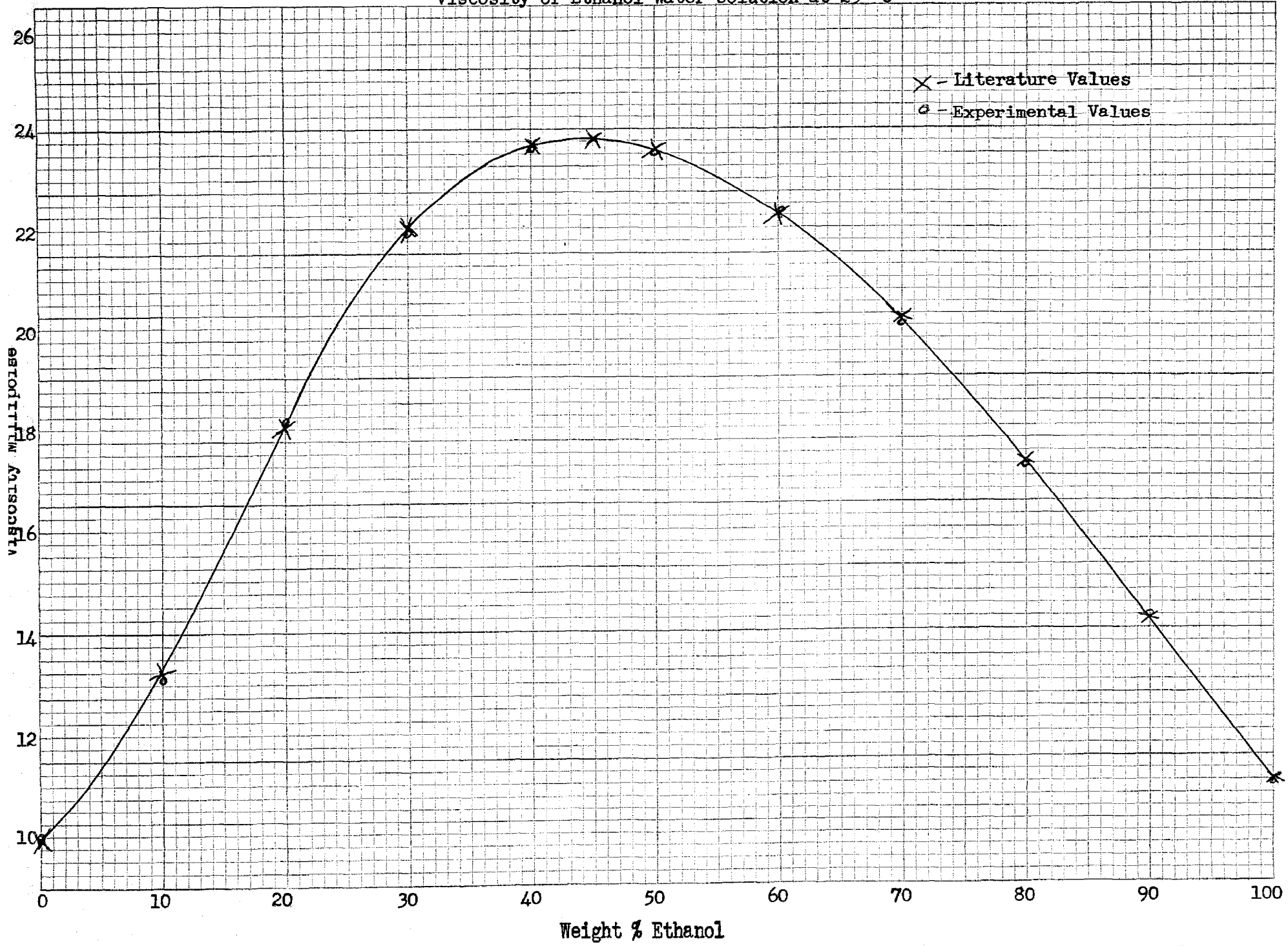
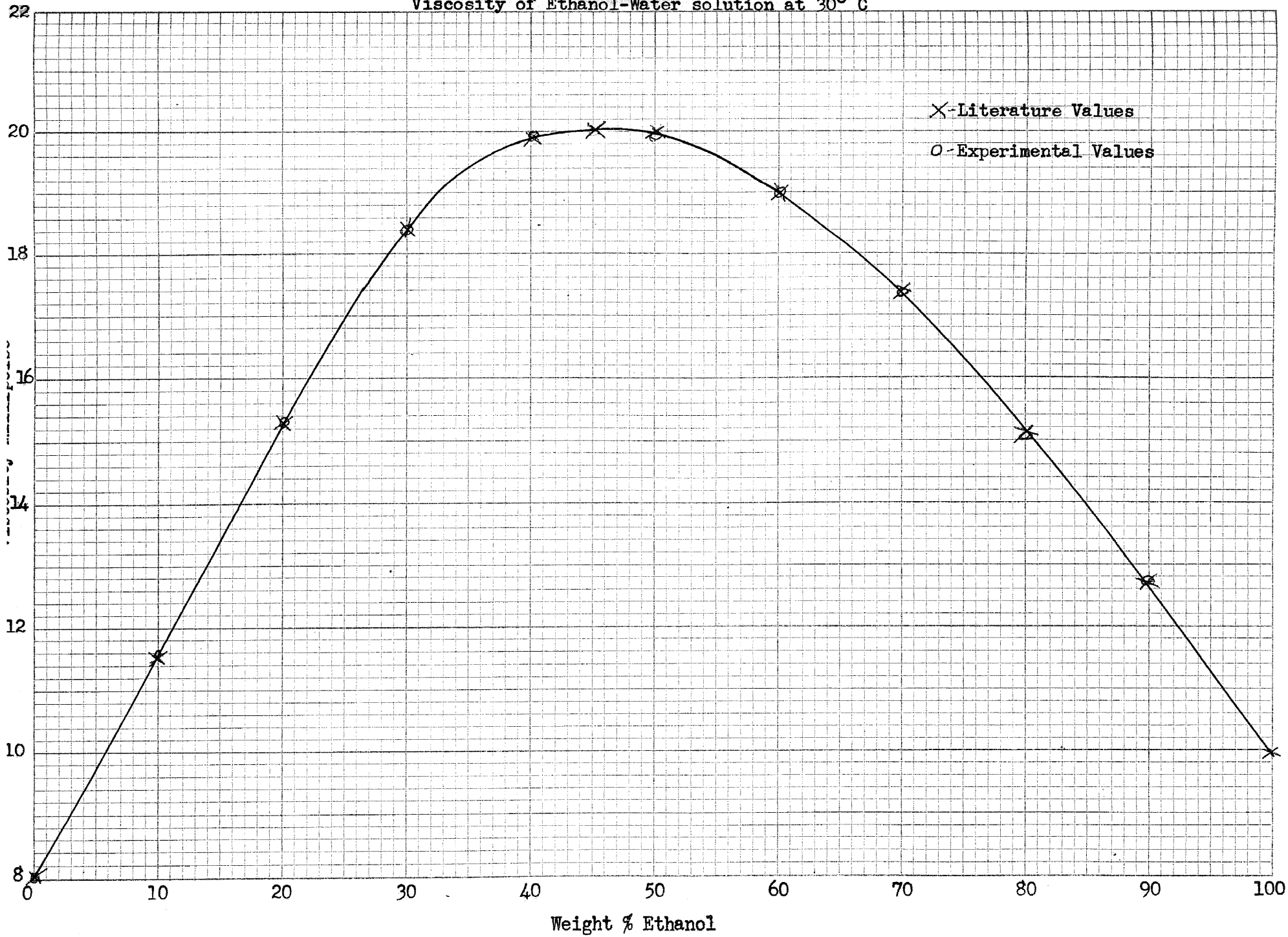
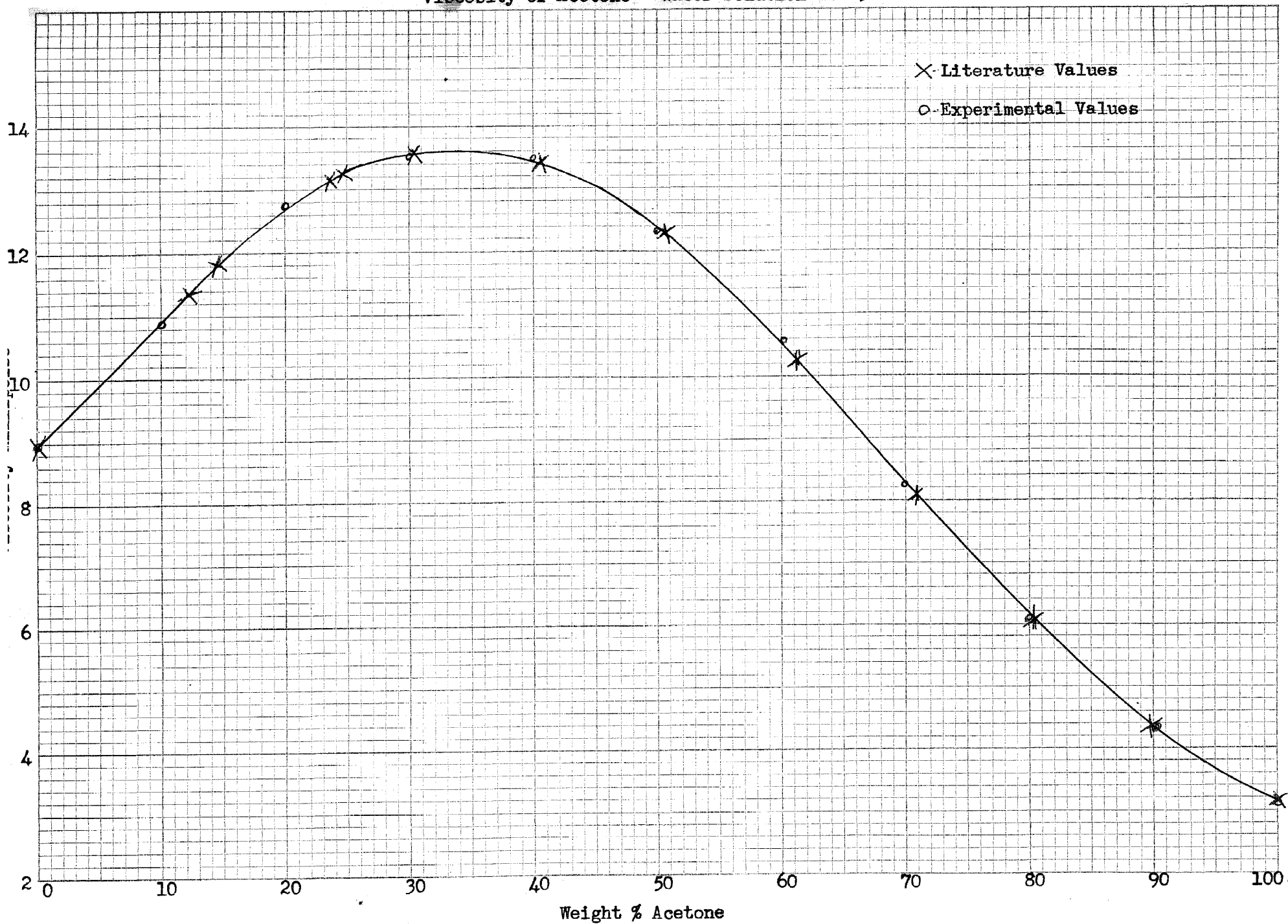


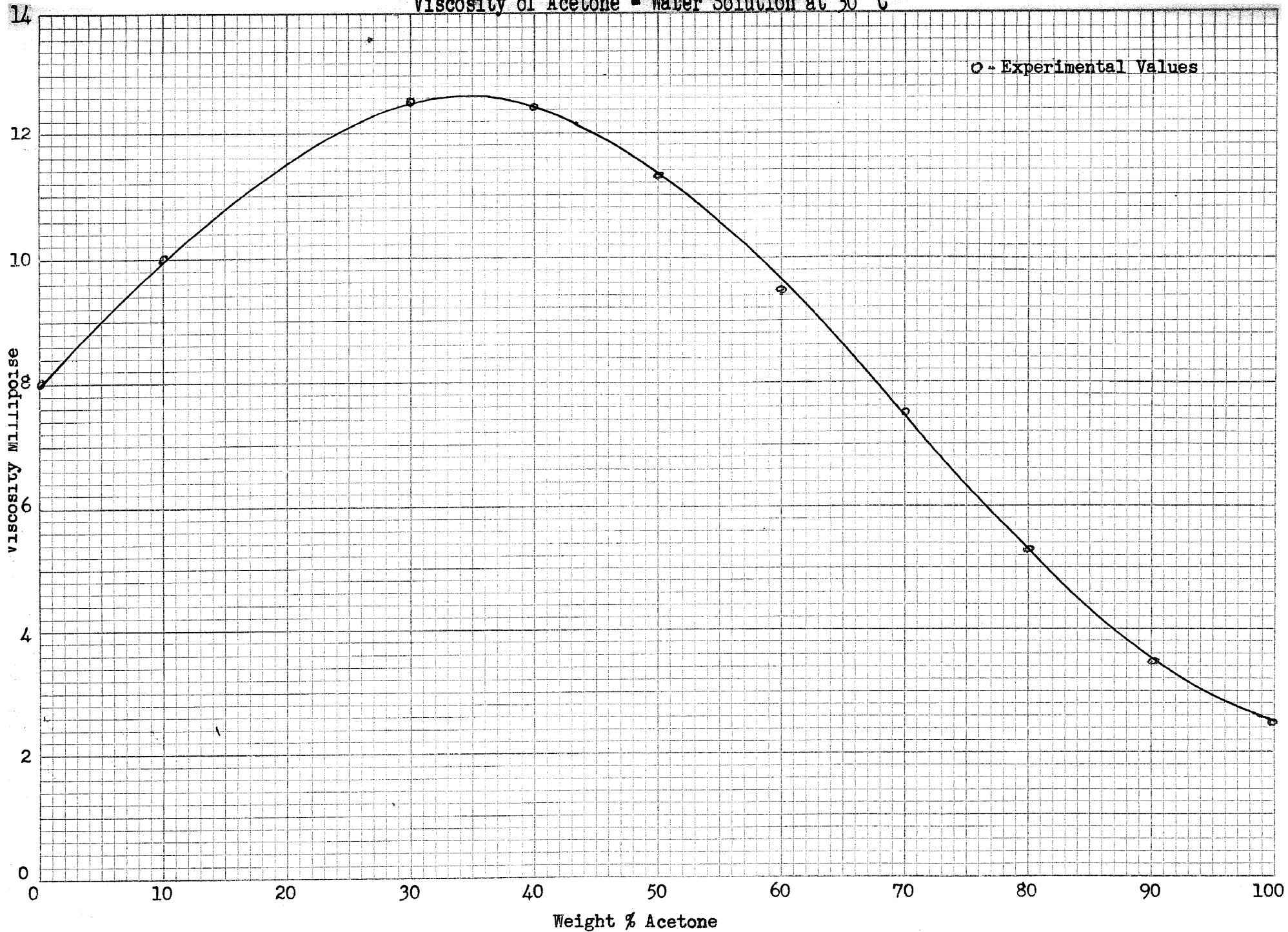
Figure 4
Viscosity of Ethanol-Water solution at 30° C



Viscosity of Acetone - Water Solution at 25° C



Viscosity of Acetone - Water Solution at 30° C



Viscosity of Acetone-Ethanol Solution at 20 °C

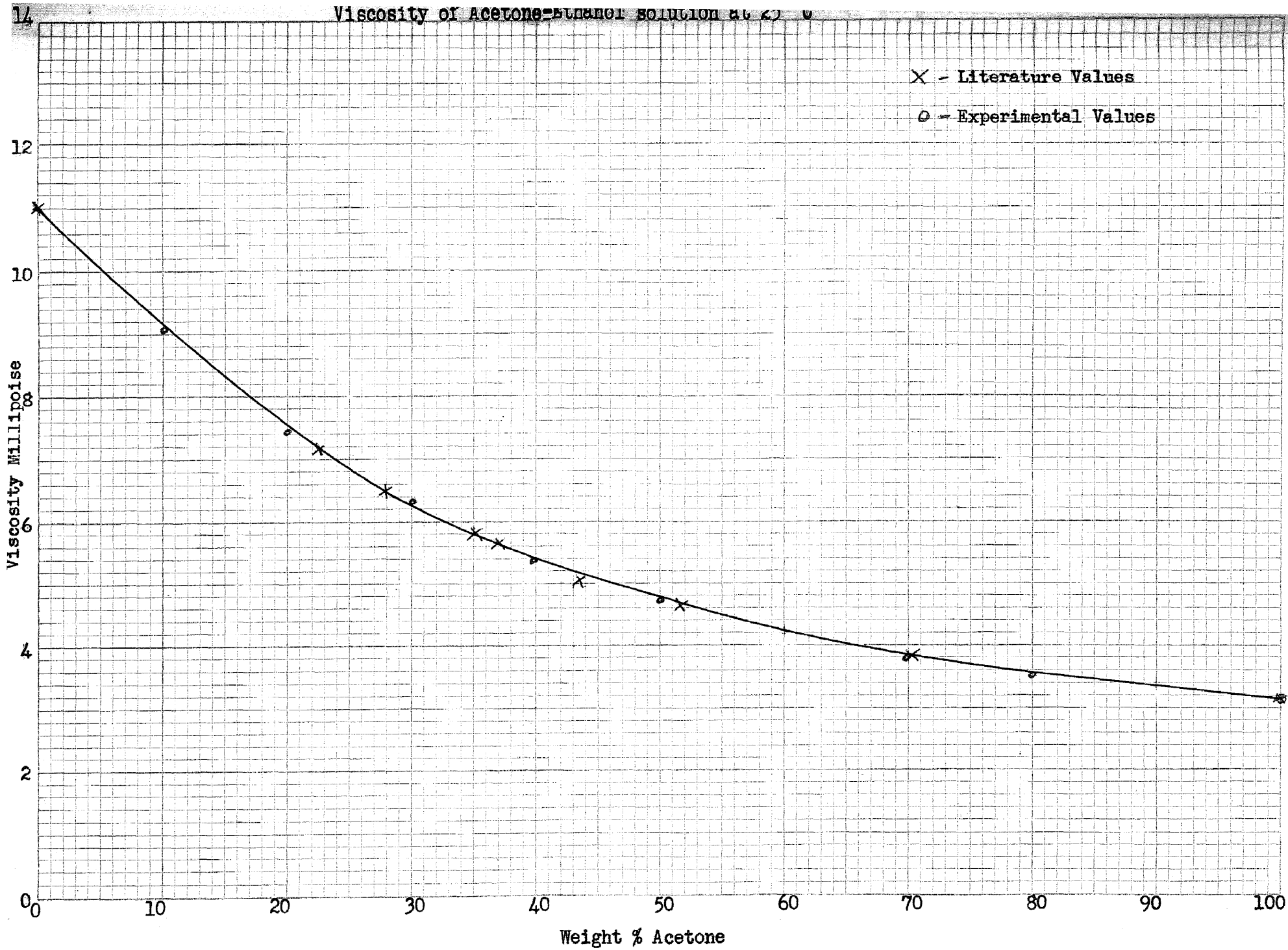


Figure 6
Viscosity of Acetone-Ethanol Solution at 30° C

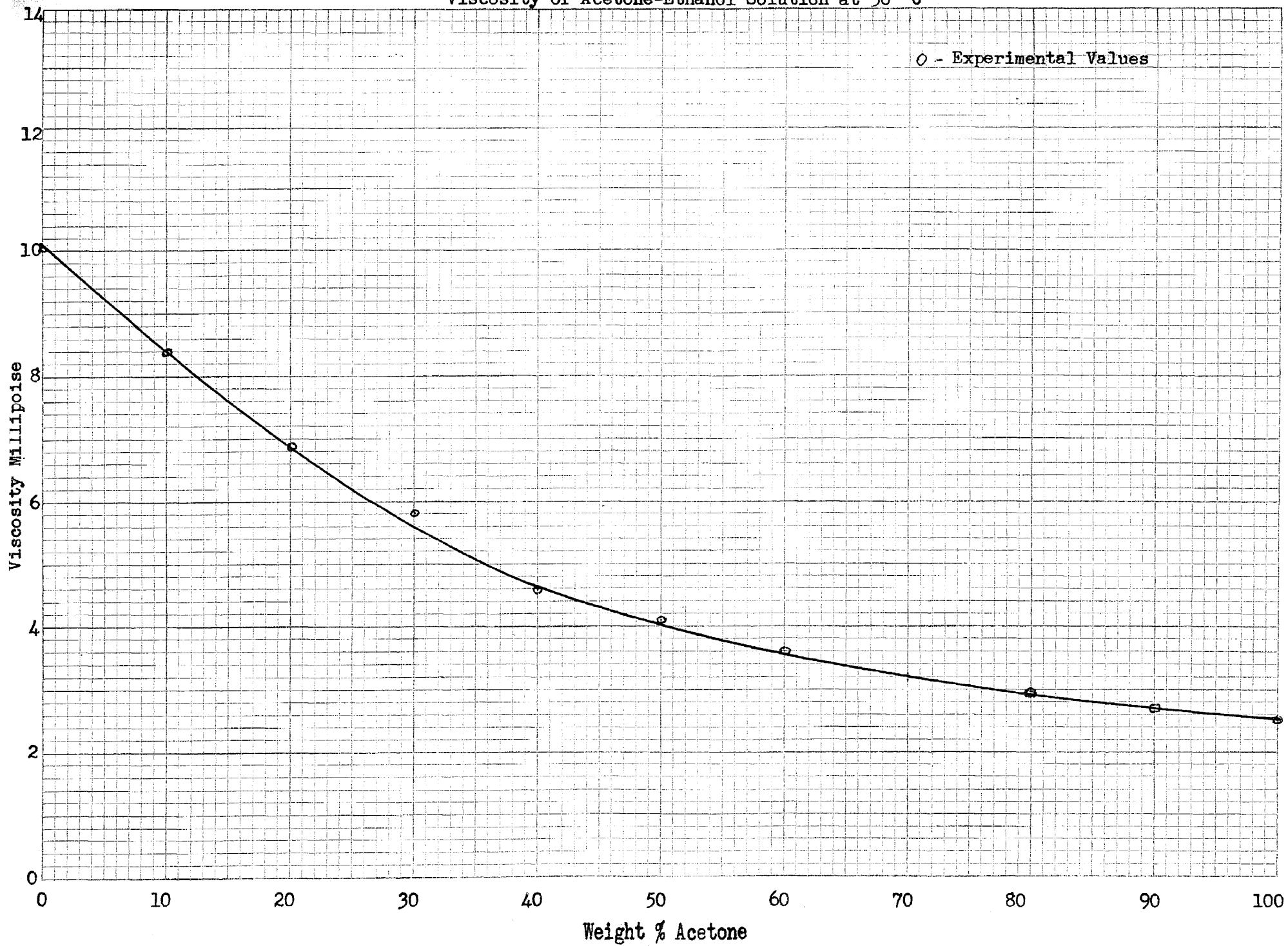


Figure 7
 Ethanol, Acetone and Water system
 Viscosities (millipoise) at 25° C
 with lines of constant viscosity

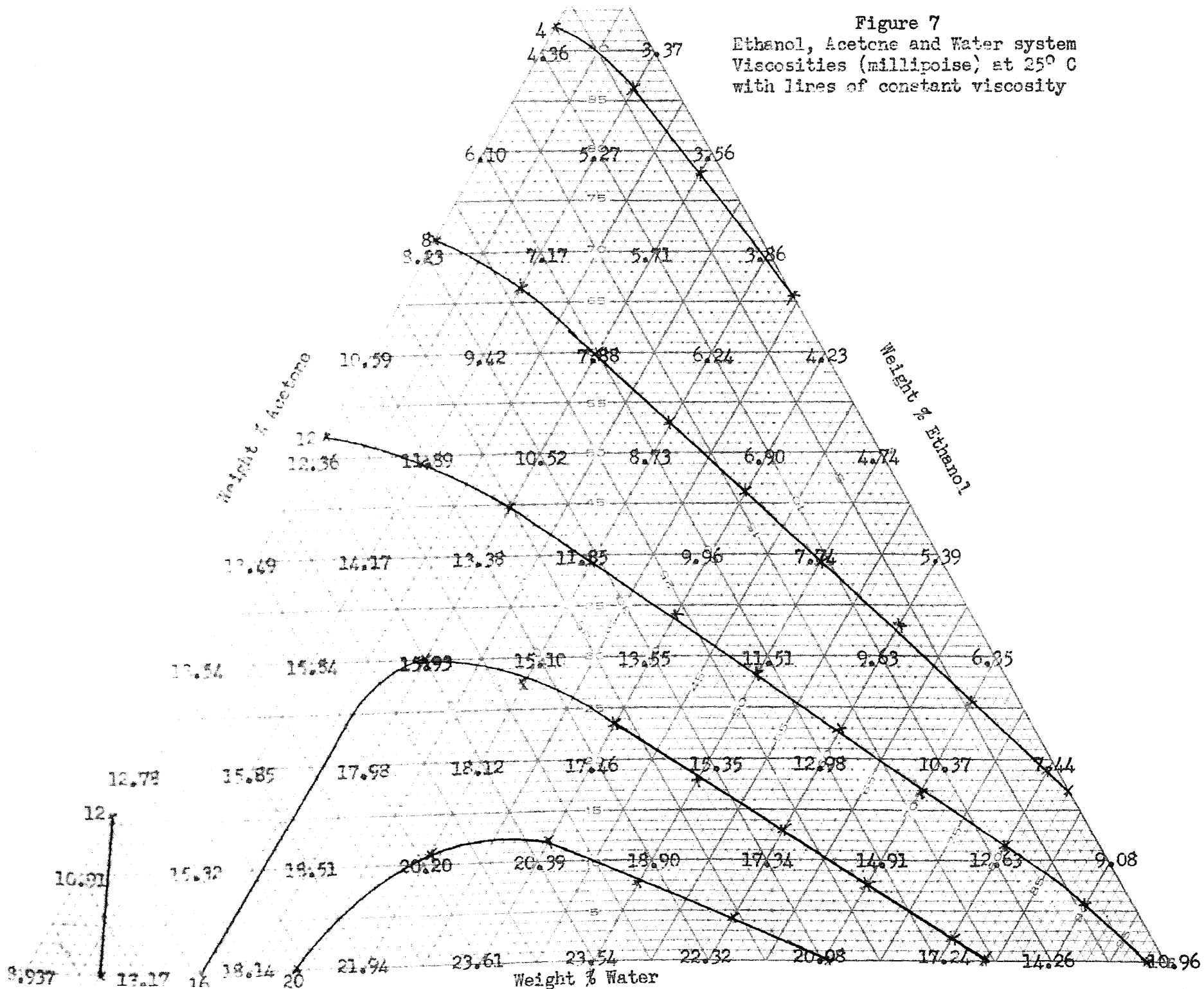
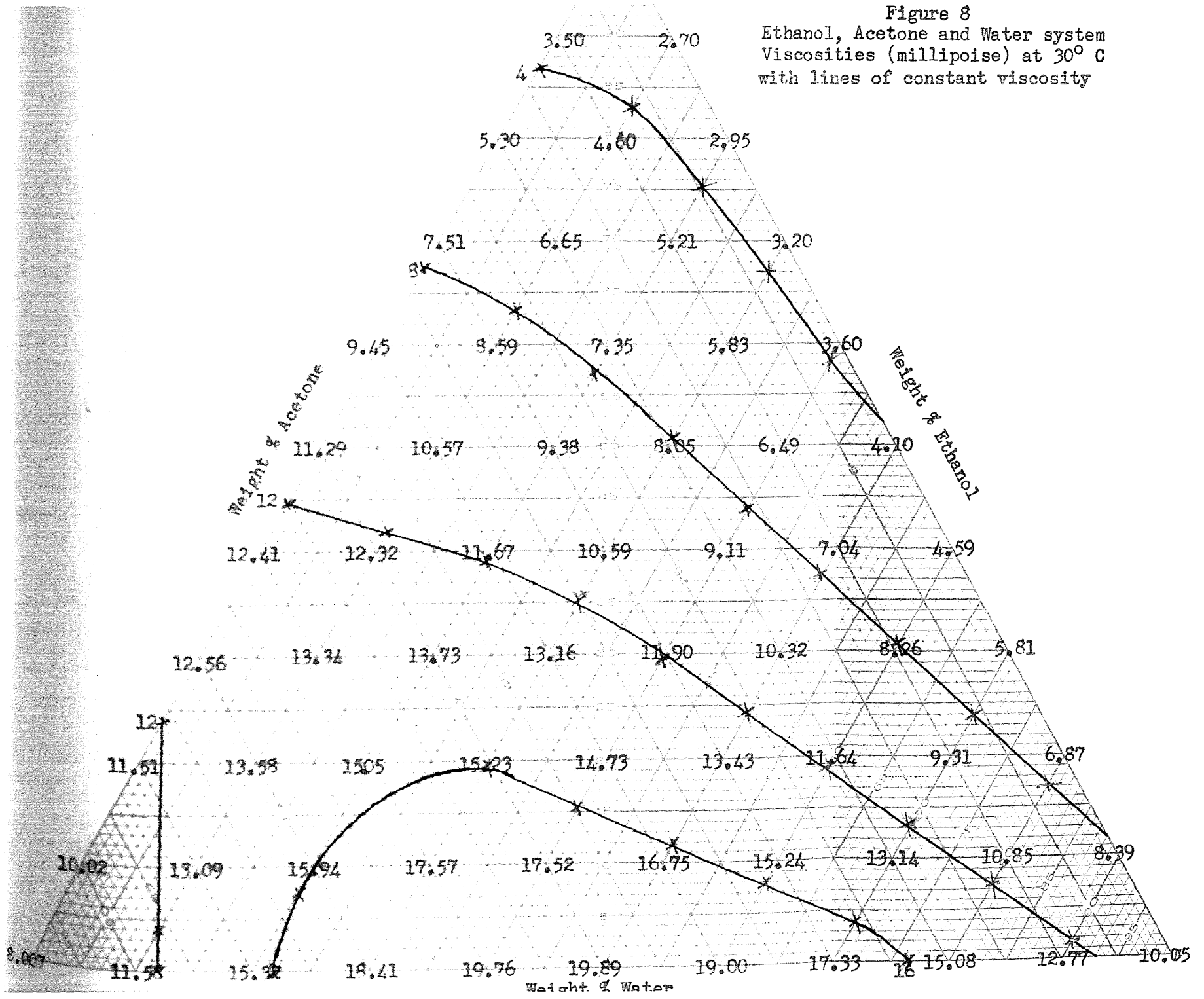


Figure 8
 Ethanol, Acetone and Water system
 Viscosities (millipoise) at 30° C
 with lines of constant viscosity



APPENDIX

CALCULATIONS

Standardization of Instruments

Pycnometer volume

Gross weight	35.4977	gms.
Tare weight	26.3822	gms.
Net weight of water (25°C)	9.1155	gms.

Absolute density of water at 25°C is 0.997044 gms/ml

therefore volume = $\frac{9.1155 \text{ gms.}}{0.997044 \text{ gms/ml}}$

= 9.1425 ml.

Calibration of #50 Ostwald-Fenske tube at 30°C (4).

For this type tube the following equation holds true.

$$V = C \times t$$

where V - viscosity in centistokes
C - the calibration constant of the instrument
t - time in seconds

further centistokes x density (d) = centipoise

therefore

$$V' = C \times t \times d$$

Where V' - viscosity in centipoise

therefore

$$C = \frac{V'}{t \times d}$$

at 30°C

V'	= 0.8937	cps.
d	= 0.995646	gms/ml
t	= 238.0	secs. average

therefore

$$C = \frac{0.8937}{0.995646 \times 238} = 0.003379$$

Determination of Sample Density

Sample 90% ethanol, 10% acetone, 0% water

Gross weight	33.5084 gm.
Tare weight	<u>26.3822 gm.</u>
Weight of sample	7.1262 gm.

$$\begin{aligned} \text{Density of sample} &= \frac{7.1262 \text{ gm.}}{9.1425 \text{ ml.}} \\ &= 0.77945 \text{ gm/ml} \end{aligned}$$

Determination of Sample Viscosity

$$V = C \times t \times d$$

where V - Viscosity in centipoise
 C - Calibration constant of instrument
 t - time in seconds, which was found to be 318.63 secs.
 d - density in gm/ml

Therefore

$$\begin{aligned} V &= 0.003379 \times 318.63 \times 0.77945 \\ &= 0.839 \text{ cps.} \\ &= 8.39 \text{ millipoise} \end{aligned}$$

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