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VISCOSITY-TEMPERATURE RELATIONS OF NAPHTHALENE IN BENZENE

by

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A thesis presented to the Department of Chemistry of
Union College in partial fulfillment of the requirements
for the degree of Bachelor of Science in Chemistry.

By Leighton H. Peebles, Jr.

Approved by Charles B. Sturd

May 26, 1949

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Introduction

A study was made of multi-benzene ring compounds dissolved in benzene in order to discover any relationship between viscosity, density, and temperature. However, as there was insufficient time, only solutions of naphthalene dissolved in benzene were studied.

Historical

Studies of binary solutions of two liquids have been performed by many workers, with many resultant equations for the viscosities. Viscosity has been used for the determination of high molecular weights and for the analysis of petroleum. Aqueous solutions have been thoroughly studied with respect to viscosity, but there remains a lot of work to be done in non-aqueous solutions. The change in viscosity with members of a family has also been studied, but not with binary solutions."

Apparatus

The densities of the solutions were determined by measuring the volumes of weighed samples in a dilatometer. A water filled electrically controlled, electrically heated thermostat was used. The temperature variations in the bath were $\pm 0.02^\circ\text{C}$. at each temperature. These fluctuations caused no measurable

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variation in the volume. The temperature was read on a calibrated Will Corporation thermometer to 0.01° by a magnifier.

The dilatometer was made by sealing a 3 mm. i.d. graduated tube to a cylindrical bulb with a capacity of approximately 24 ml. The volume could be read to an accuracy of ± 0.001 ml. Standard methods of weighing the sample and calibrating the dilatometer with distilled water were used. The dilatometer was calibrated to ± 0.003 ml. at each temperature used, and the final calculated densities were ± 0.0002 , or two parts in 10,000.

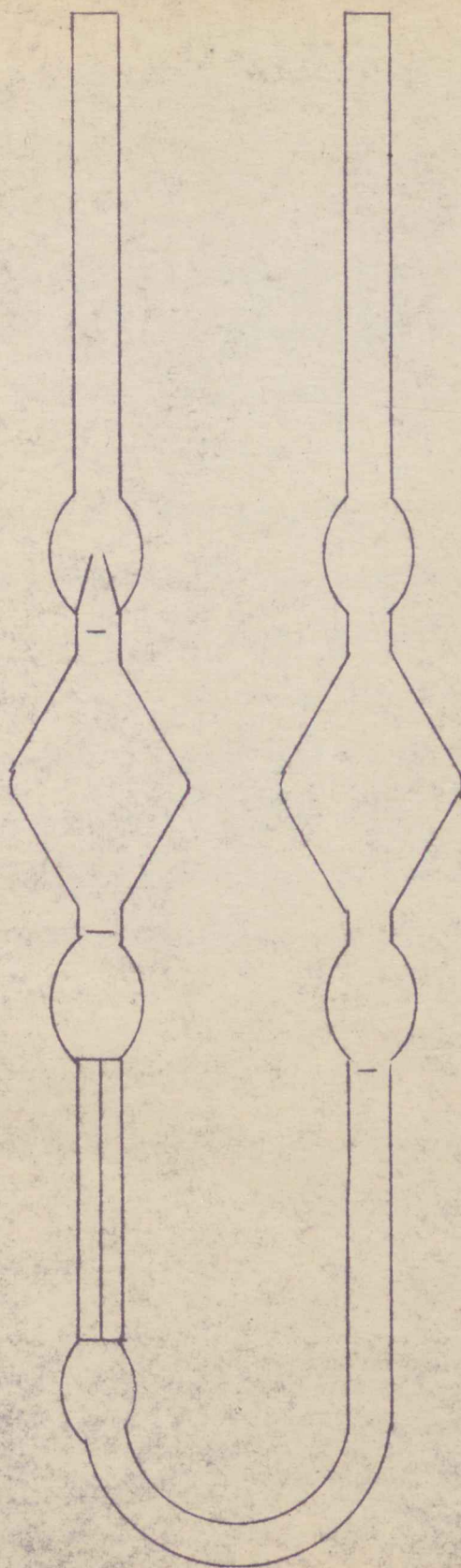
The viscosities were determined by the method of Bingham.³ See Fig. I. The pipette used was calibrated by standard liquids from the Bureau of Standards by the General Electric Company and was checked by me with benzene. The values obtained fell between values previously reported.^{2,10} The formula used was:

$$\eta = C \sqrt{p} - C' \rho / t \quad (1)$$

The constants were $C = 9.010 \times 10^{-5}$, $C' = 1.43$. Where " ρ " is the density; " p " is the pressure or height of water in centimeters corrected to 25° read as hydrostatic pressure on a metal scale; and " t " is the time in seconds measured by an electric timer. The pressure was obtained from a laboratory air line and stored in a large tank sufficiently lagged to prevent sudden pressure drops due to thermal change. Stopcocks were arranged so that pressure could be applied to one side of the pipette while the other was open to the atmosphere. All determinations required the liquid to flow first down the left hand side, then down the right hand side of the viscometer. Each

Fig. I

Viscosity Pipette



determination was checked immediately and the largest variation between two runs was twelve parts in 10,000 and the average deviation was about seven parts in 10,000. The thermostat previously described was used.

It was found that if the time was not long enough during a viscosity determination, the calculated results did not check if the pressure was varied, temperature being held constant, as the estimate of error due to time was too high. Time used for all determinations was over 400 seconds, preferably around 500 seconds. It was also found that the apparatus could not be operated on a windy day as the manometer was open to atmospheric pressure which would change. Also as the equipment was in a small room, all doors in the room and in adjoining rooms had to be kept open as the closing of a door would cause a pressure change. This probably had no effect on the results except that the manometer could not be read immediately after a pressure change as the water column vibrated. Fifteen minutes or longer was always allowed for the solutions to come to constant temperature when placed in the bath.

Purification of Materials

The benzene was purified by the method of Weissberger¹⁶ by drying reagent thiophene-free benzene with sodium, then distilling from sodium. Resublimed naphthalene was crystallized twice from absolute methyl alcohol. Its melting point was 79.5°.

to 30.5°.

Preparation of Solutions

Solutions were prepared by weight in narrow mouthed, glass stoppered bottles. The empty bottle was weighed and weighed again after receiving a roughly weighed sample of naphthalene. A third weight was taken after the benzene was admitted. Weights were corrected to vacuum.

The solutions evaporated somewhat from the dilatometer as some time usually passed between determinations, so the amount of naphthalene in the dilatometer was calculated and assumed to remain constant and the dilatometer was weighed before and after each determination.

Experimental Results

Table I

Viscosities of benzene-naphthalene solutions in centipoises
Concentration expressed in per cent by weight of naphthalene

°C	0%	9.974%	20.106%	32.441%
25	.6041	.6668	.7436	.8643
30	.5633	.6215	.6905	.7982
35	.5267	.5798	.6419	.7417
40	.4936	.5413	.5997	.6903
45	.4643	.5095	.5626	.6456
50	.4369	.4793	.5285	.6064

Table II

Densities of benzene-naphthalene solutions. Concentration expressed as per cent by weight of naphthalene.

°C	conc.	dens.	conc.	dens.	conc.	dens.	conc.	dens.
25	0	.8730	9.974	.8667	20.233	.9011	33.441	.9198
30	0	.8678	9.974	.8618	20.121	.8958	33.444	.9149
35	0	.8624	9.974	.8764	20.122	.8907	33.445	.9099
40	0	.8569	9.974	.8710	20.123	.8854	33.446	.9049
45	0	.8515	9.974	.8657	20.109	.8803	33.434	.9001
50	0	.8460	9.974	.8605	20.106	.8753	33.435	.8951

Discussion of Results

The densities were plotted as isotherms against concentration (Fig. II) on large coordinate paper and found to be linear within experimental error. In Table III are the constants for the variation of density of pure benzene with temperature using the equation:

$$d_t = d_{25} + a(t - 25) + b(t - 25)^2 + c(t - 25)^3 \quad (2)$$

Table III

$$d_{25} = .8730$$

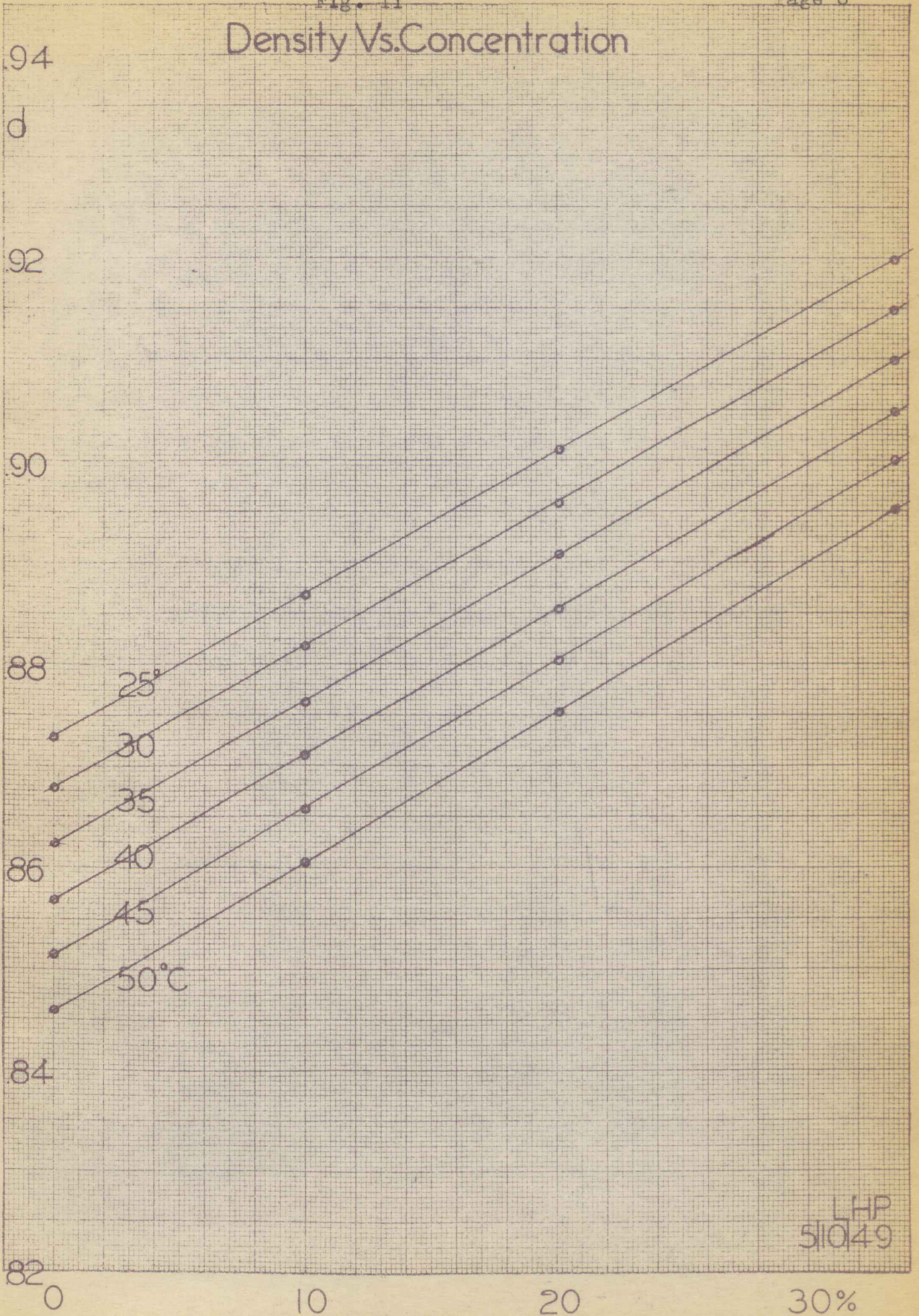
$$a = -1.043 \times 10^{-5}$$

$$b = -1.922 \times 10^{-6}$$

$$c = +2.095 \times 10^{-8}$$

where "d" is the density and "t" is degree Centigrade. These values are good to one part in 10,000.

Density Vs. Concentration



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The variation of density with concentration follows the equation:

$$d_c = mC + d_t \quad (3)$$

where " d_c " is the density at a given concentration and temperature; " m " is the slope of the line; " C " is the concentration in per cent by weight; and " d_t " as determined by Equation (2). " m " and " d_t " were determined by the method of least squares and " d_t " was generally 0.0001 unit less than those given in Table II. The slope of the lines increased gradually as shown by the increase in " m ".

Table IV

Constants of Equation (3)

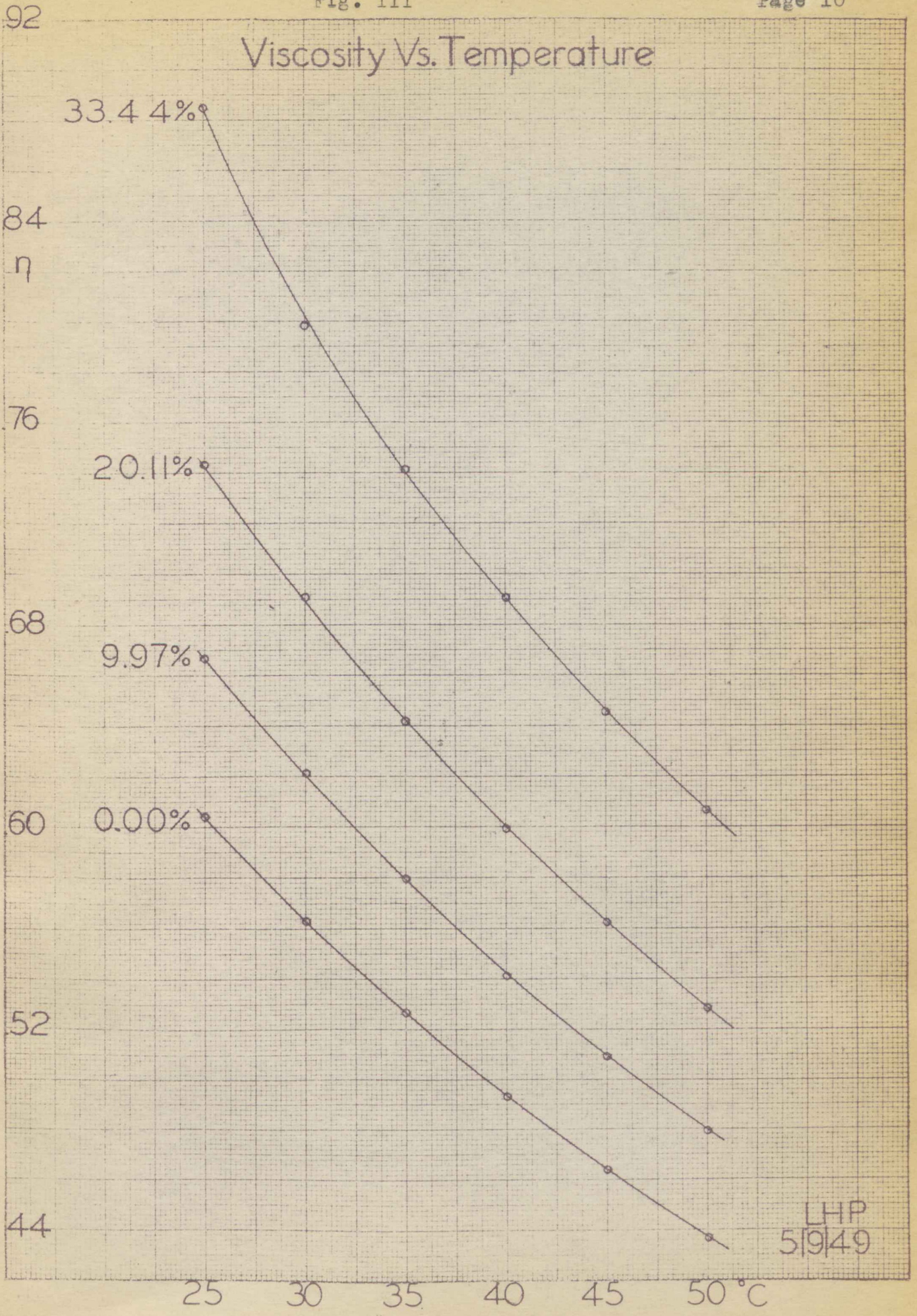
" d_t " as determined by method of least squares, " d_t^1 " from Table II, and " d_t^{11} " from Equation (2).

$^{\circ}C$	d_t	d_t^1	d_t^{11}	m
25	.8729	.8730	.8730	1.40
30	.8677	.8678	.8678	1.41
35	.8623	.8624	.8626	1.42
40	.8569	.8569	.8570	1.43
45	.8515	.8515	.8516	1.45
50	.8459	.8460	.8460	1.46

Equation (3) in conjunction with Table IV and Equation (2) gives values good to six parts in 10,000.

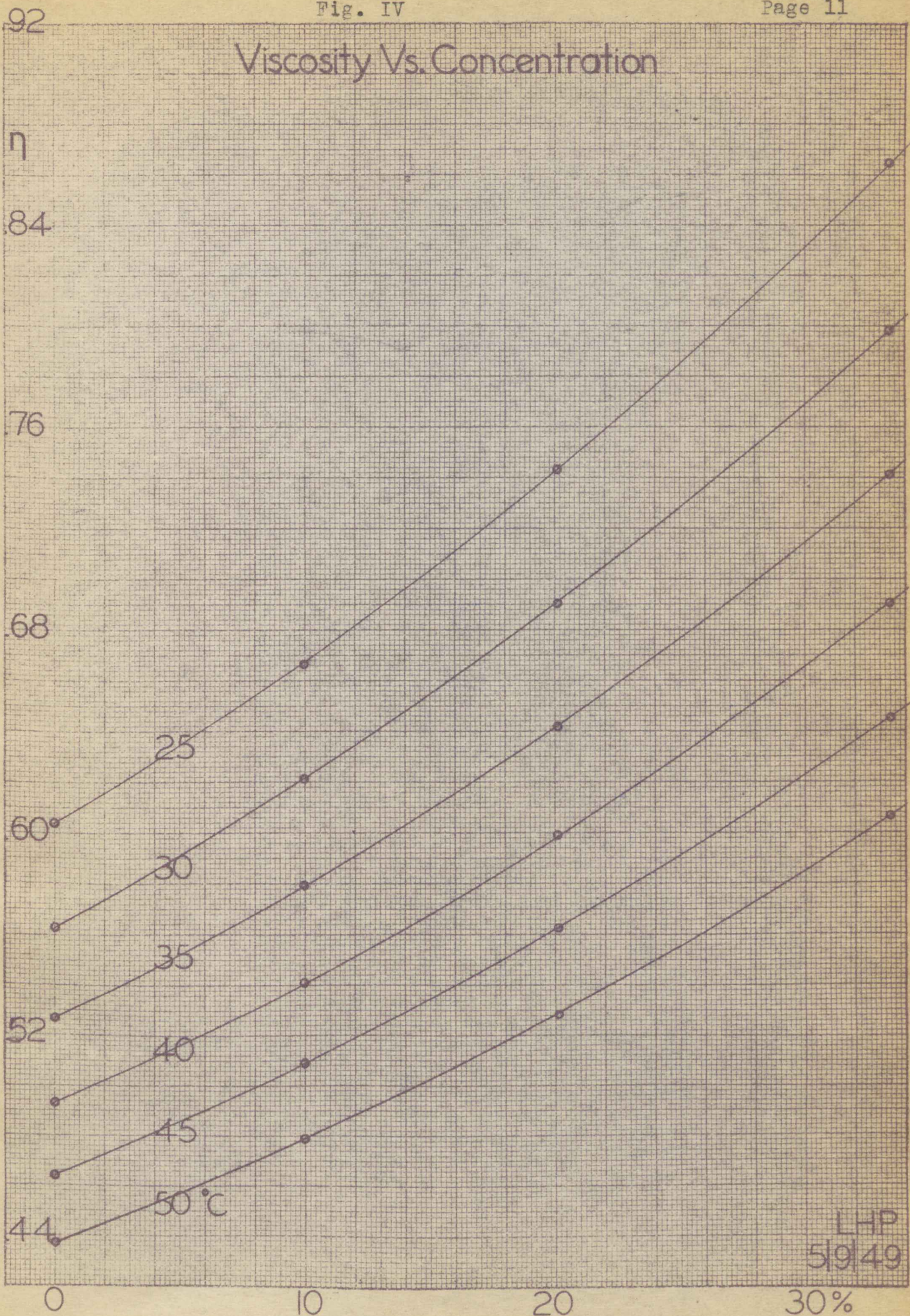
The viscosity data were plotted in four ways: Viscosity against Temperature (Fig. III); Viscosity isotherms against concentration in per cent by weight (Fig. IV); Logarithm of Viscosity against Reciprocal Absolute Temperature (Fig. V); and the

Viscosity Vs. Temperature



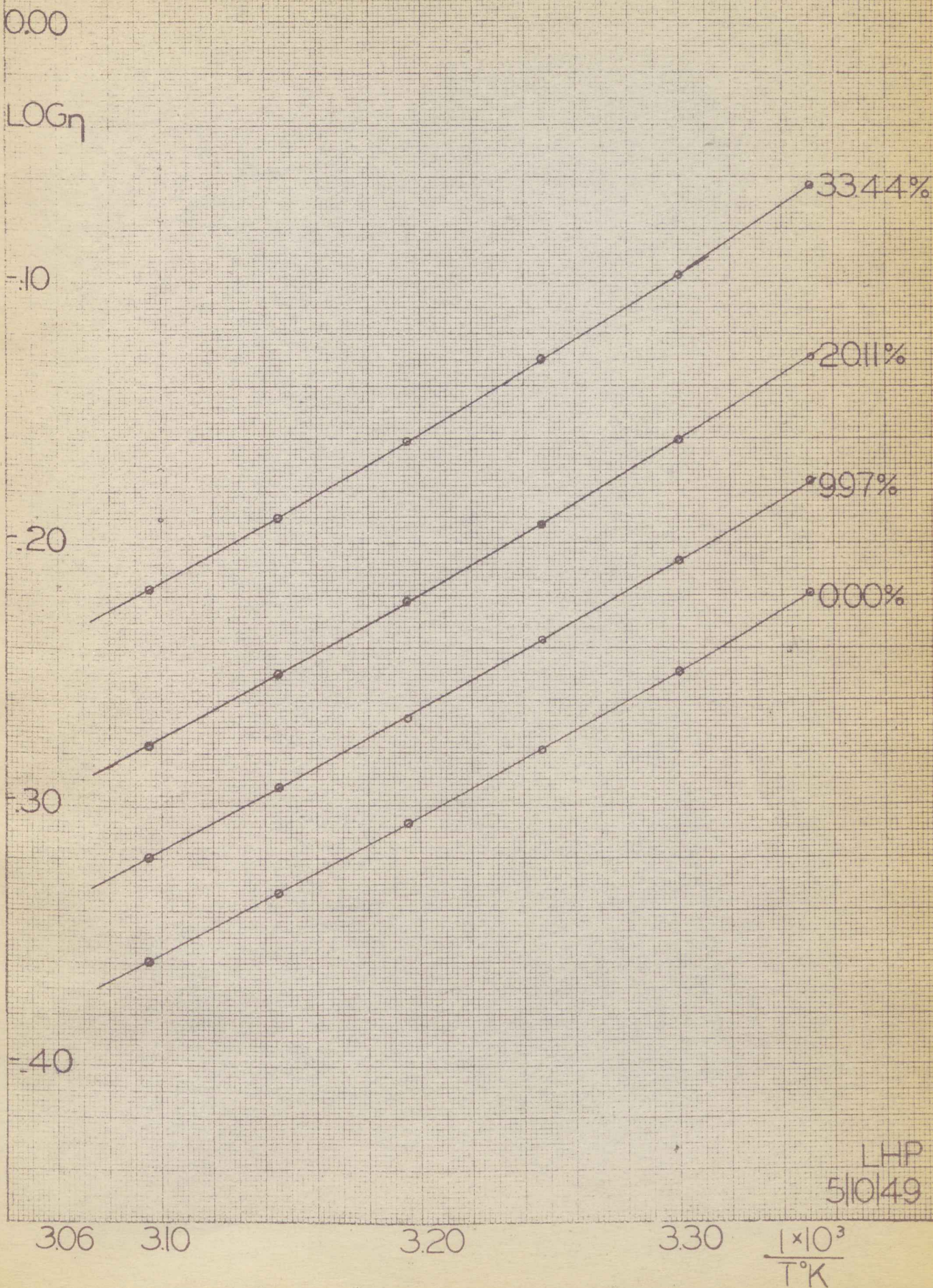
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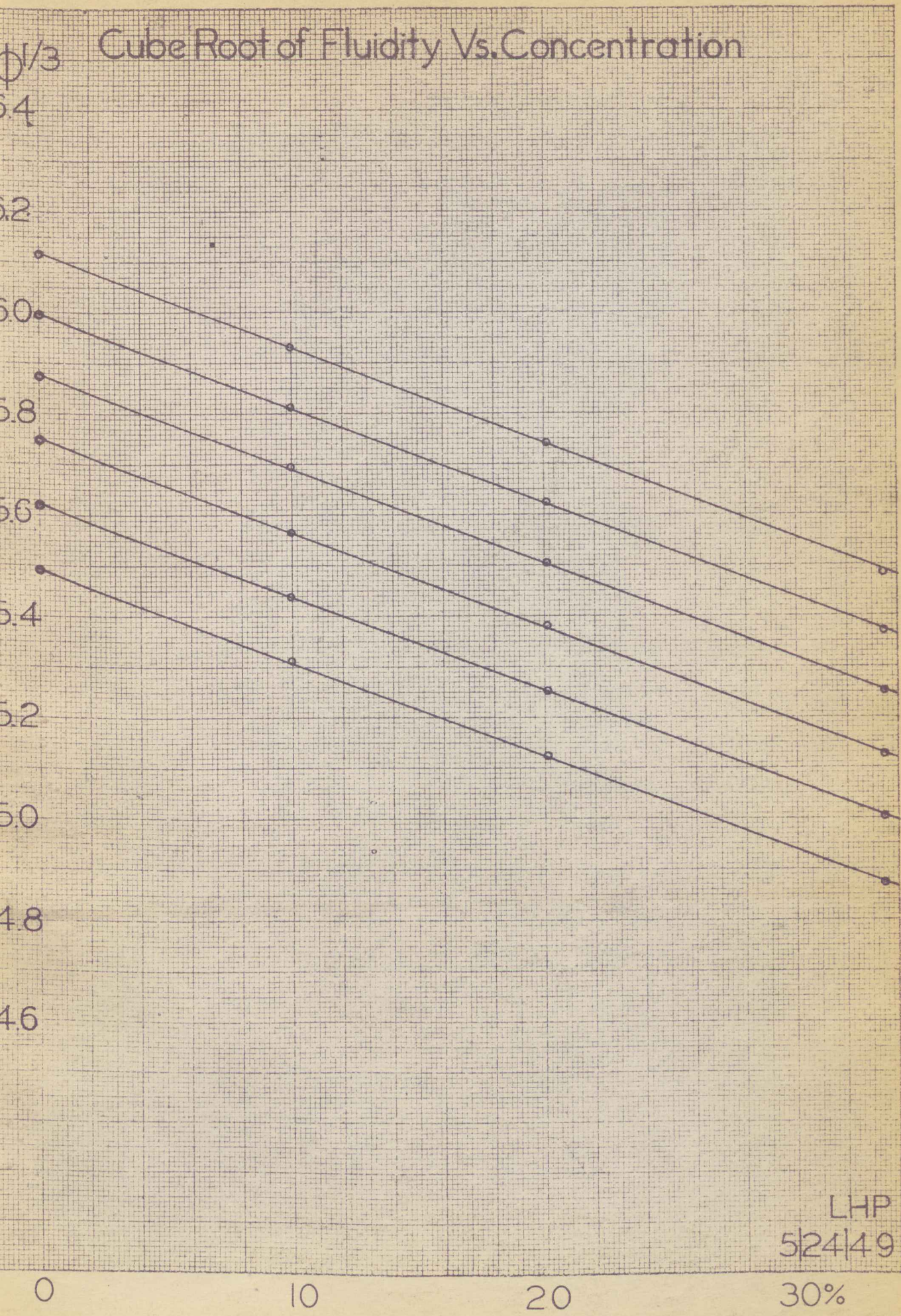
Viscosity Vs. Concentration



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Log Viscosity Vs. Reciprocal Absolute Temperature





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Cube Root of Fluidity or Reciprocal Viscosity expressed in poises against Concentration expressed as per cent by weight (Fig. VI).

The log of viscosity against $1/T \cdot R$ (Fig. V) was plotted on large coordinate paper and found not to be linear, but with a slight curvature. This curvature prevents the use of the equation:

$$\log \eta = B/T + A \quad (4)$$

or the more recent formula:⁷

$$\log \eta = Q_1/2.30 RT + A \quad (5)$$

where Q_1 is called the energy of activation of viscous flow. The curves would probably obey the equation:

$$\log \eta = Q_1/2.30 RT + A + CT \quad (6)$$

This indicates that Q_1 is not a constant but increases slightly with an increase in temperature. The energy of activation of viscous flow can be determined by finding the constants of Equation (6) and taking the derivative $d\eta/dT$, substituting in T and multiplying by $+2.30 R$ where "R" is the molar gas constant expressed in calories. All concentrations including pure benzene showed non-linearity, whereas most liquids when plotted in this manner do obey Equations (4) and (5).

In (Fig. III), viscosity against temperature, the curve for pure benzene did not follow the equations of Batschinski² or any of those reviewed and postulated by Bingham.⁴ The curve does follow the equation:

$$\eta = a + bt + ct^2 + dt^3 \quad (7)$$

Table V
 Constants for Equation (7)

$$\begin{aligned} a &= +.9006 \\ b &= -1.559 \times 10^{-2} \\ c &= +1.727 \times 10^{-4} \\ d &= -9.333 \times 10^{-7} \end{aligned}$$

the constant "a" would probably be the viscosity of benzene at 0°C if its freezing point were below zero. This is in fair agreement with the value .9002 cp. previously reported, the calculated value for benzene at zero. The value for undercooled benzene given by Thorpe and Rodgers in 1894 at zero degrees is .906 cp.⁸

Equation (7) deviates from the data as the temperature increases and at 50°C is good to 14 parts in 10,000. The maximum possible error for benzene is ± 0.0004 cp. at 25°C or seven parts in 10,000.

Lantle¹³ said that ideal binary mixtures indicate that the cube root of fluidity (reciprocal viscosity in poises) can be expressed as a linear function of the mol ratio. This was found not to be true but it is a linear function if the concentration is expressed as per cent by weight:

$$\phi_0^{1/3} = mC + \phi_t^{1/3} \quad (8)$$

where " ϕ_0 " is the fluidity at a given concentration and temperature; "m" is the slope of the line; "C" is the concentration in per cent by weight of naphthalene; and " ϕ_t " is the fluidity, $1/(\eta \times 10^{-2})$, of pure benzene, as determined by Equation (7).

The constants "m" and " $\phi_t^{1/3}$ " were determined by the method of least squares.

Table VI

Constants of Equation (8)

" $\phi_t^{1/3}$ " determined by the method of least squares, " $\phi_t^{1/3'}$ " calculated from Table I, " $\phi_t^{1/3''}$ " calculated from Equation (7).

$^{\circ}\text{C}$	$\phi_t^{1/3}$	$\phi_t^{1/3'}$	$\phi_t^{1/3''}$	m
25	5.494	5.491	5.491	-1.65
30	5.521	5.520	5.520	-1.64
35	5.750	5.748	5.748	-1.65
40	5.875	5.873	5.875	-1.66
45	5.997	5.994	5.997	-1.67
50	6.118	6.117	6.121	-1.69

The value for "m" at 25° has been checked and is correct.

Exactly why the slope should change as it does is unknown.

It must be remembered when considering ideal solutions, a liquid dissolved in a liquid, and a solid dissolved in a liquid are not quite the same because of the large difference in freezing points. Many formulas and theories have been suggested concerning the viscosity of binary liquids, taking into account factors such as association factor¹²; contraction or expansion in volume upon mixing¹; change in density⁵; free space and ratio of apparent and actual molecular weights¹⁴; and barriers around molecules in the liquid¹⁵ but most of these are concerned with functions of the viscosities or fluidities of the pure substances, and cannot be in this case.

Summary

From these data, I concluded that for ideal or near ideal solutions, the density can be expressed as a linear function of concentration in per cent by weight. The cube root of fluidity can be expressed as a linear function of concentration in per cent by weight. The energy of activation of viscous flow is not constant, but increases slightly with increase in temperature.

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Leighton H. Peebles, Jr.