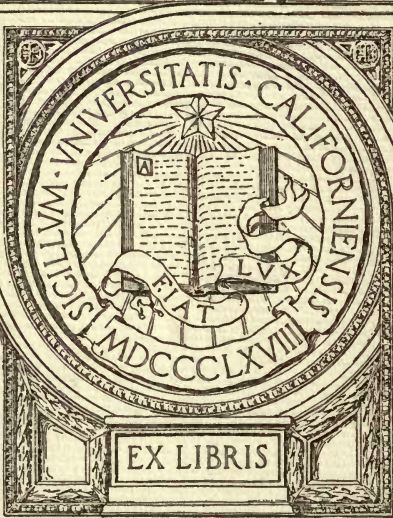


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# The Viscosity of Liquids

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## IV. Ideal Liquid Mixture of the Types Ether-Ether and Ester-Ester

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DISSERTATION

SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIRE-  
MENTS FOR DEGREE OF DOCTOR OF PHILOSOPHY IN  
THE FACULTY OF PURE SCIENCE OF  
COLUMBIA UNIVERSITY

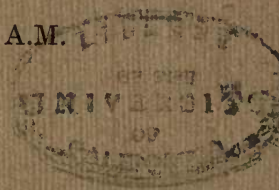
BY

ALEXANDER HOLLAND WRIGHT, A.M.

NEW YORK CITY

June, 1920

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The Jackson Press, Kingston  
1920



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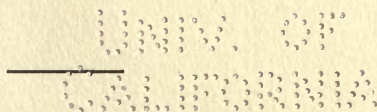
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*Contents*—1. Introduction. 2. Review of previous work. 3. Object of this investigation. 4. Experimental procedure. 5. Formula for absolute viscosity. 6. Correction of the pressure for the liquid "head." 7. Choice and preparation of substances used. 8. Experimental data—Series of the Ethers A . . C, Series of the Esters D . . F. Resume of the experimental data. 9. Other possible formulae. 10. Summary.

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### ACKNOWLEDGMENT


To Professor James Kendall, at whose suggestion this problem was undertaken, the author wishes to express his sincere gratitude for help and advice during the progress of the work.

To Professor Thos. B. Freas, and the other officers of the Chemistry Department of Columbia, the author also desires to extend thanks for coöperation.

Nichols Laboratories of Inorganic Chemistry,

Columbia University, June, 1920.





## The Viscosity of Liquids.

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### IV. Ideal Mixtures of the Types: Ether-Ether and Ester-Ester.

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#### 1. INTRODUCTION

The need for greater knowledge of viscosity of liquids has been noted by Kendall<sup>1</sup> and by Kendall and Monroe<sup>2</sup> in the previous papers of this series.

The continual refinement of method in determining other physical properties of substances, for use in the study of chemical constitution and in all lines of chemical research, has urged the authors of this paper to continue their efforts to advance, in like manner, our knowledge of the viscosity of liquids.

The need for further research upon this subject is the more apparent when we consider the large use now being made of viscosity as a physical property for the determination of the presence of and identification of compounds in mixtures such as in airplane "dopes", oil mixtures, etc.

It is axiomatic that any results derived from such uses of this property are conditioned by our only approximate knowledge of the physical meaning of viscosity and the nature of the molecular forces existing in liquids. Our ideas are still rather vague regarding the nature of the forces affecting viscosity in the liquid state.<sup>3</sup> A very great deal of work has been put on the study of ideal solutions without as yet yielding us an ideal equation for such solutions.

<sup>1</sup>For the first article of this series, see Kendall, *Medd. K. Vetenskapssakad, Nobelinst.*, 2, No. 25 (1913).

<sup>2</sup>For the second and third articles, see Kendall and Monroe, *J. A. C. S.*, 39, 1787 (1917).

<sup>3</sup>A differentiation between viscous flow in liquids and in gases has been attempted by Bingham, *J. A. C. S.*, 36, 1393 (1914).

Probably some fundamentally important factor (such as change in internal pressure or average molecular volume with composition of the mixture) has not been brought into consideration. Many other such factors readily occur to one in considering conditions which must exist when molecules of different structure and weight pass by one another in the flow of liquids.

## 2. REVIEW OF PREVIOUS WORK

Attempts to derive an ideal equation for mixtures have been made in the previous papers of this series. In the first paper Kendall tested all proposed formulae by means of the available data and he concluded that a modification of a formula

$$[(\eta = \eta_1^x \cdot \eta_2^{(1-x)})]$$

in which ( $\eta$ ) is the viscosity of the mixture, ( $\eta_1$ ) and ( $\eta_2$ ) are the viscosities of the components, while ( $x$ ) was a factor of the concentration of the components] proposed by Arrhenius<sup>4</sup> gave more satisfactory results than the others. This formula has the logarithmic form of  $\log \eta = x \log \eta_1 + (1-x) \log \eta_2$ , in which ( $\eta$ ) has the same meaning as in the formula of Arrhenius but ( $x$ ) has values in terms of molecular percentage.

This formula was later the object of special investigation at the Nobel Institute of Physical Chemistry by Hans Egner<sup>5</sup> under the direction of Professor Svante Arrhenius. The results in every way confirmed what Kendall found concerning the usefulness of the various formulae, closing with the statement that the modified logarithmic formula of Arrhenius and Kendall "represents the variation of the viscosity in binary liquid mixtures of the normal type more exactly than any other formula proposed."

The tabulation of data upon the viscosity of substances by the monograph of Dunstan and Thole<sup>6</sup> and the perfection of the new apparatus of Bingham<sup>7</sup>, by which measurements of viscosity in absolute units could be obtained more accurately and quickly than by

<sup>4</sup>See Arrhenius, *Zeitschr. phys. Chemie*, 1, 285 (1887). See also Arrhenius, *Medd. K. Vetenskapsakad. Nobelinst.* 3, No. 13 (1916), where the same formula is shown to apply to suspensions of colloids.

<sup>5</sup>Hans Egner, *Medd. K. Vetenskapsakad. Nobelinst.* 3, No. 22 (1917).

<sup>6</sup>Dunstan and Thole, "The Viscosity of Liquids," Longmans (1913).

<sup>7</sup>Bingham, *J. Ind. Eng. Chem.* 6, 233 (1914); Bingham, Schlesinger and Coleman. *J. A. C. S.* 38, 27, (1916). See also Washburn and Williams, *Ibid.* 35, 737 (1913).

the old Ostwald type of viscosimeter, gave a great stimulus to all work along this line.

In the second and third papers of this series, Kendall and Monroe reviewed the previous work done on viscosity and again tested by their own experimental data the proposed formulae for ideal binary mixtures. They found no agreement with any formula, since the logarithmic viscosity-molecular composition formula gave results varying from 6.8 to 27 per cent less than experimental values, while the logarithmic viscosity-weight or volume composition equation deviated to even a larger degree. Thus while the logarithmic viscosity-molecular composition formula was the best of all previously proposed, it gave results far in excess of experimental error or possible deviation from ideality. The cube root formula which they suggested gave much closer agreement (See Table III c, Benzene-Benzyl Benzoate),<sup>8</sup> but even this fails with one of the systems (Table VI, Toluene-Benzyl Benzoate) and gives discordant results for their solid-liquid systems. Thus in the Benzene-Benzyl Benzoate system, Kendall and Monroe got better results with the cube root formula, while with the Toluene-Benzyl Benzoate, the results were not so good.

### 3. OBJECT OF THIS INVESTIGATION

Results obtained in a conductivity research by Kendall and Gross indicated that benzyl benzoate, as obtained by Monroe, was not perfectly pure.<sup>9</sup> It was consequently hoped that additional data, with widely separated components and purer material, might render possible an ultimate decision as to the validity of the cube root formula for representation of experimental results.

In this, the fourth paper of this series, the aim is, primarily, to secure data that give a wider range of variation of the viscosities

<sup>8</sup>See Kendall and Monroe, *loc. cit.*, p. 1803.

<sup>9</sup>Benzyl benzoate used by Kendall and Monroe gave a m.p. 18.8° and a viscosity of 0.08454. That used by the present authors was specially prepared and purified by repeated fractional distillations under low pressure, in a new piece of apparatus devised by Gross and Wright for maintaining a constant known low pressure during fractional distillation where the receiver can be changed without changing the pressure. The sample used in this research gave a m.p. 19.4; b.p. 323 ± .2, no conductivity, and a viscosity of 0.08514.

See Berkeley, J. C. S. 109, 520 (1916), on difficulty of preparing benzyl benzoate.

of the components of the mixture, and, secondarily, to test out with these data the two formulae suggested by Kendall and Monroe in their paper. In the third place, it was the hope to narrow down still further the possible range between which the true formula for these ideal mixtures lies. The authors believe that they have accomplished all three of the objects for which they began their work.

#### 4. EXPERIMENTAL PROCEDURE

The apparatus used in determining the viscosities was the same as that used by Kendall and Monroe. The same methods of determining pressure and time intervals were used. This apparatus was in large measure that devised by Bingham.<sup>10</sup>

The viscosimeters used were of the type devised by Bingham. In these, the capillary tube is divided into two parts by a widened portion of the tube, with the transpiration volumes of about 3.5 c.c. at each outer end of the capillaries, the entire tube being shaped like a "U."

A definite volume is obtained in each measurement by pouring into one side of the tube an approximate volume. The liquid is then drawn up the other side by the pressure in the manometer so as to completely fill the two capillaries, the connecting portion between these and the one transpiration volume, up to a trap at the upper end of the left side of the tube. The excess liquid, beyond a definite volume, is poured over into the trap.

A low pressure reservoir was connected to the viscosimeter, water manometer and filter pump. Constant pressure was insured throughout an experiment by careful adjustment of the pressure in the water manometer by means of two reservoirs. The aim was to keep the pressure, during a series of readings, constant. Readings of the pressure, whatever they were, could be taken to 0.1 c.c. on the water manometer.

After the viscosimeter was filled, it was clamped upright in a thermostat whose temperature was maintained during a series of measurement at  $25 \pm 0.02$  degrees centigrade. The Beckmann thermometer used was frequently compared with a 25 degree thermometer reading to 0.01 degrees that had been standardized by the United States Bureau of Standards.

<sup>10</sup>Bingham, loc. cit., p. 234.

When a measurement was made, the liquid was drawn down through the capillaries and filled up the transpiration volume of the other side. The time of flow of the liquid, under the known pressure of the manometer, was that required to move from one mark on the tube to another. This interval of time was taken by means of a high grade stop watch which was read accurately to the tenth of a second.<sup>11</sup>

By this method, a definite volume of about 3 c.c. of the liquid was permitted to flow through the two capillaries each time a measurement was taken. After the one side of the tube had been emptied, this same side was refilled by the liquid flowing back through the capillaries in the reverse direction under the known pressure. These two sets of readings,—the one emptying and the other filling the left side of the tube,—were kept by themselves and the averages of the time intervals and the pressure measurements were taken for the best reading of each side for each sample of each mixture.

These "best readings" of the time and pressure were set down in the formula for the absolute viscosity as will be indicated in fuller detail below. The value of the viscosity of a sample, as outlined above, was repeated with new lots of the same mixture and the average of these values was taken as the final value of the viscosity of that particular mixture. Three trials, at least, were made to obtain each value for the absolute viscosity of the one proportion of the two components being used at the time.

These three trials must agree with each other or they were rejected and a new lot of the components were made up in that proportion.

All precautions were taken to keep all apparatus clean and dust free. After each measurement, the viscosimeter was thoroughly cleaned and dried by a current of dust free air.

In preparing each mixture, definite weights of each component were mixed in a standardized narrow necked 20 c.c. volumetric flask. Any change of volume was carefully watched for, as well as any change of temperature, when the mixture was shaken together. From the weights of each component, the molar proportions and the density of each mixture were obtained at 25°C. Components were at 25°C. before mixing as well as when taking density

<sup>11</sup>The stop watch used here was the same one that had been used by Kendall and Monroe. Its accuracy was tested at frequent intervals by an expert horologist.

determinations, volume changes and temperatures of the mixtures. all mixtures were stored away from the light as well as from change in temperature.

An approximate volume of the well-shaken mixture was put into the viscosimeter, in which the liquid, after coming to equilibrium in the thermostat, was drawn to the trap side so that the approximate volume became a definite volume by the loss of the excess by overflowing into the trap. Thus at the beginning of each measurement, the entire left side of the "U" shaped viscosimeter was filled with the liquid from the tip of the fine inner tube at the trap down through the two capillaries and the lower part of the "U", which connects the two capillaries, up the right side of the viscosimeter to the exact point where the right hand capillary stops at its upper end. When the measurement is to be made, the connection with the manometer is opened so that pressure due to the hydrostatic column in the manometer, will be exerted upon the liquid on the left side forcing the liquid through the two capillaries. When the liquid had just passed a certain line on the left side of the tube, the stop watch was started, and when the liquid had passed through the two capillaries so that its height on the left side had fallen to a certain definite line, the watch was stopped. The time interval was read from the watch and the same procedure was repeated in the reverse direction. The hydrostatic column of water was expressed in grams and recorded as pressure for that single "run." The value of the pressure and time for each sample were placed in the simplified formula for viscosity, as will be shown in what follows in more detail, and thus two or three values for the absolute viscosity of that particular mixture must check to be finally accepted.

Two different viscosimeters were used, one for the more viscous, the other for the less so. These viscosimeters were standardized by taking readings with water <sup>12</sup> in the same manner as with the mixtures as indicated above. The value of the absolute viscosity of water at 25°C. was taken as  $\eta=0.008946$ .<sup>13</sup>

## 5. FORMULA FOR ABSOLUTE VISCOSITY

The complete formula used for each viscosimeter in determination of the absolute viscosity was the following:—

<sup>12</sup>This water was redistilled in pyrex flasks, first from alkaline permanganate and then again by itself and stored away from air.

<sup>13</sup>See Kendall and Monroe, *loc. cit.*, p. 1794, Note 4.

$$\eta = \frac{\pi g r^4 p t}{8 V l} - \frac{1.12 n \rho V}{8 \pi t l}.$$

where ( $g$ ) is the acceleration due to gravitation; ( $r$ ) is the radius of the capillaries; ( $V$ ) is the transpiration volume, (the volume in c.c. of liquid that flows through the capillaries in the time the liquid is falling between the two marks on the left side of the tube); ( $l$ ) is the length of each capillary (average of the two if any difference is noted); ( $n$ ) is the number of the capillaries; ( $\rho$ ) is the density of the liquid. This formula was simplified into the form,

$$\eta = C p t - C_1 \rho / t$$

by substituting  $C$  for

$$\frac{\pi g r^4}{8 V l} \text{ and } C_1 \text{ for } \frac{1.12 n V}{8 \pi l}$$

$C_1$ , which is the term for the kinetic energy correction, is usually of very small value<sup>15</sup> and can be obtained with sufficient accuracy for each viscosimeter by direct measurement. Then the value of  $C$  can be obtained for each instrument by standardization with water at 25° by taking  $\eta = 0.008946$  as the value of the absolute viscosity of water and substituting it in the above simplified formula. This standardization was cross checked, one value of  $C$  and  $C_1$  against another by using other liquids (as ethyl benzoate) so as to eliminate any errors. When the values of  $C$  and  $C_1$  were finally obtained, they were used continually for the particular tube to which they belonged.

## 6. CORRECTION OF THE PRESSURE FOR THE LIQUID "HEAD."

Each pressure reading was modified in accordance with the recommendation of Bingham, Schlesinger and Coleman.<sup>16</sup>

This correction was made because the true average pressure ( $p$ ), driving liquids through the viscosimeter, is not equal to the observed manometer reading ( $p_0$ ), but was given by the relation

<sup>14</sup>See Dunstan and Thole, "The Viscosity of Liquids," p. 2; also Bingham and White, loc. cit, pp. 681-3.

<sup>15</sup>For one viscosimeter the following value was obtained for this second term of the simplified formula: 0.000098187, and for the other instrument the value of 0.00009677 was found.

<sup>16</sup>See Bingham, Schlesinger and Coleman, J. A. C. S. 38, 27 (1916).

$$p = 2 h \rho / \log_e \frac{p_0 + h \rho}{p_0 - h \rho}$$

where ( $h$ ) is the maximum head of the liquid in the viscosimeter; ( $p_0$ ) the observed manometer pressure, and ( $\rho$ ) is the density of the mixture. Kendall and Monroe<sup>17</sup> have shown the significance of this correction and that, with this correction, values of  $C$  are obtained for each viscosimeter that are constant for the various pressures, used in the various measurements, made with each instrument. When the various pressures are thus corrected, they are placed in the simplified formula and values, thus obtained, for the viscosity of any one liquid, at the different pressures, check each other. This last fact is also shown in the above mentioned paper of Kendall and Monroe.

## 7. CHOICE AND PREPARATION OF SUBSTANCES USED

The substances chosen for use by the present authors, in obtaining data of mixtures that would give a wide range of viscosity of the components, were representatives members of the ethers and esters.

The choice of material was based on the desire to provide ideal mixtures of components with a wide range of viscosity. The substances used are:

(a) of essentially the same character, hence there were no compound formations;

(b) non-associated, hence no disassociation on admixture;

(c) widely separated in molecular weight, viscosity and density, thus allowing of a definite choice between the different formulae to be tested.

In the ethers, the differences in molecular weight are either once or twice 48, while in the esters, the differences are once or twice 62. In the viscosities, the ethers vary from 0.002283 to 0.03864; while the esters vary from 0.00423 to 0.08514. In density, the ethers varied from 0.76 to 1.0756 and the esters from 0.899 to 1.1147.

All the chemicals were purified by fractional crystallization, as in the case of diphenyl ether, or by repeated fractional distillation, using an apparatus especially devised for this sort of work by Gross and Wright.

<sup>17</sup>See Kendall and Monroe, loc. cit., p. 1795.



This apparatus will be the subject of a separate paper, entitled, "Distillation Apparatus." The distillations were repeated under low pressure that was nearly constant, known in amount and not subject to big change, as is usually the case in changing receivers in repeated fractional distillations. This permitted corrections to be made on the boiling points of each fraction and enabled better separations to be made. The distillations were continued until fractions were obtained with the same physical constants.

The first three series of mixtures were made with ethers as follows:

Series A—diethyl ether and phenetole.<sup>18-19</sup>

Series B—diethyl ether and diphenyl ether.<sup>20</sup>

Series C—phenetole and diphenyl ether.

The second set of three series were mixtures of esters, as follows:

Series D—ethyl acetate and ethyl benzoate.<sup>21-22</sup>

Series E—ethyl benzoate and benzyl benzoate.<sup>23</sup>

Series F—ethyl acetate and benzyl benzoate.

## 8. EXPERIMENTAL DATA

The data for the series of the ethers are presented first. The first column gives the molecular proportions of the components; the second column, the experimental value of the absolute viscosity of each mixture; columns three and four give values of the viscosity calculated from the modified Arrhenius formula of logarithmic viscosity-molecular composition and the percentage differences from

<sup>18</sup>The ethyl ether used was washed with small amounts of water, then with solution of  $\text{Na}_2\text{CO}_3$ , dried for several months over metallic sodium and fractionally distilled. Portion used gave b.p.  $34.6^\circ\text{C}$ .; sp. g.  $25/4^\circ\text{C}$ . of 0.714.

<sup>19</sup>The phenetole was fractionated by the Gross and Wright apparatus. Portion used gave b.p.  $170.1^\circ\text{C}$ . and sp. g.  $25/4^\circ\text{C}$ . of 0.962.

<sup>20</sup>The diphenyl ether was fractionated under low pressure and finally fractionally crystallized many times. m.p.  $27-27.1^\circ\text{C}$ .

<sup>21</sup>The ethyl acetate was washed with small amounts of water, solution of  $\text{Na}_2\text{CO}_3$ , dried over  $\text{P}_2\text{O}_5$ , fractionated with the Gross and Wright apparatus, b.p. of portion used  $77.1-77.2^\circ\text{C}$ . No conductivity.

<sup>22</sup>The ethyl benzoate was washed, dried over  $\text{CaCl}_2$ , fractionated repeatedly, b.p. of portion used was  $209.1^\circ\text{C}$ .

<sup>23</sup>This benzyl benzoate was very specially prepared and purified with repeated fractionations. No conductivity; m.p.  $19.4^\circ\text{C}$ .; b.p.  $323 \pm 0.2^\circ\text{C}$ ., and a viscosity of 0.08514.

the experimental values. The last two columns give similar results derived from the calculations of the viscosity of the mixture from those of the components by the use of the empirical formula suggested by Kendall and Monroe, called the cube root formula. The results will be discussed in detail below.

**SERIES A. MIXTURES OF DIETHYL ETHER AND PHENETOLE.**

Molar fraction of ethyl ether.	$\eta$ (Exp)	Log. visc.	Diff. %	Cube root	Diff. %
1.0000	0.002233	.....	....	.....	....
.9004	.002674	.002646	-1.1	0.002757	+3.0
.8303	.003057	.002952	-3.4	.003171	+3.7
.7485	.003494	.003377	-3.3	.003704	+6.0
.6882	.003944	.003730	-5.4	.004133	+4.8
.6048	.004406	.004278	-2.9	.004780	+8.5
.5579	.004809	.004629	-3.8	.005176	+7.6
.5106	.005154	.004996	-3.0	.005587	+8.3
.4501	.005713	.005519	-3.3	.006151	+7.7
.3516	.006667	.006489	-2.7	.007148	+7.2
.3026	.007152	.007035	-1.6	.007682	+7.4
.2523	.007856	.007642	-2.7	.008256	+5.1
.1855	.008671	.008530	-1.6	.009274	+7.0
.0975	.009993	.009860	-1.3	.01025	+2.5
.0745	.01027	.01024	-.2	.01052	+2.4
.0000	.01158	.....	....	.....	....

This system was ideal by all the tests that we could make. No heat or any volume changes could be detected. The results indicate that the logarithmic formula gives values rather closer to the experimental than does the cube root formula.

**SERIES B. MIXTURES OF DIETHYL ETHER AND DIPHENYL ETHER.**

Molar fraction of ethyl ether.	$\eta$ (Exp)	Log. visc.	Diff. %	Cube root	Diff. %
1.0000	0.002233	.....	....	.....	....
.9092	.003106	.002893	- 6.8	0.003344	+ 7.3
.7826	.004552	.004150	- 8.8	.005433	+19.3
.7088	.005733	.005122	-10.6	.006978	+21.3
.6076	.007614	.006835	-10.2	.009539	+25.3
.5102	.009926	.009022	- 9.0	.01253	+26.0
.4245	.01258	.01152	- 8.4	.01563	+24.0
.3297	.01631	.01509	- 7.5	.01962	+20.2
.2193	.02153	.02068	- 3.9	.02505	+16.3
.1318	.02737	.02654	- 3.0	.03000	+ 9.6
.0704	.03158	.03161	+ 0.1	.03382	+ 7.0
0.0000	.03864	.....	....	.....	....

So far as our measurements would indicate, this system is ideal. No change of volume or any indication of evolution of heat upon dissolving of one liquid in the other could be detected. Again the results indicate superiority of the logarithmic viscosity formula over the cube root.

This is the best system of all the ethers because of the long range of variation of the viscosity of the components. That of diphenyl ether is nearly eighteen times as great as that of ethyl ether. This system gives us a better indication of the value of the two formulae than will either of the other two systems of the ethers.

#### SERIES C. MIXTURES OF PHENETOLE AND DIPHENYL ETHER.

Molar fraction of phenetole.	$\eta$ (Exp)	Log. visc.	Diff. %	Cube root	Diff. %
1.0000	0.01158	.....	....	.....	....
.9006	.01309	0.01305	-0.3	0.01337	+2.1
.8127	.01451	.01451	0.0	.01510	+4.1
.7037	.01632	.01654	+1.4	.01745	+6.8
.6002	.01822	.01879	+3.0	.01990	+9.2
.5105	.02096	.02088	-0.4	.02218	+5.8
.3731	.02455	.02460	+0.2	.02602	+6.0
.3253	.02630	.02611	-0.7	.02748	+4.5
.2072	.03003	.03012	+0.3	.03127	+4.1
.1367	.03264	.03277	+0.4	.03363	+3.1
0.0000	.03864	.....	....	.....	....

This system is ideal as shown by the lack of any indication of volume change or evolution of heat when the two components were mixed. The results, here as in all the systems of the ethers, as calculated by the logarithmic formula are slightly more according to the facts than in the case of the cube root formula.

Figure one shows, graphically, the three curves for each system. This figure is self-explanatory and brings out in a better way the relative agreement of the logarithmic formula and the cube root formula.

#### THE SYSTEMS OF THE ESTERS

The data for esters are given below. The same order is maintained here as in the case with the ethers.

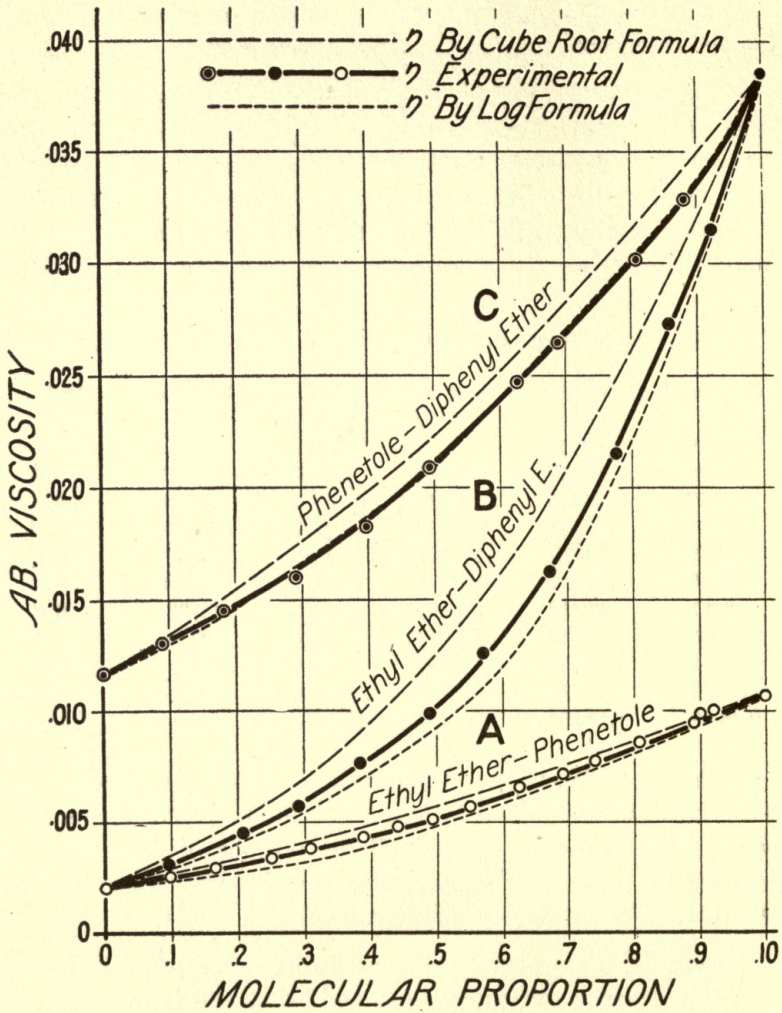


Fig. No. 1

SERIES D. MIXTURES OF ETHYL ACETATE AND ETHYL BENZOATE.

Molar fraction of ethyl acetate.	$\eta$ (Exp)	Log. visc.	Diff. %	Cube root	Diff. %
1.0000	0.004239	.....	....	.....	....
.8992	.005188	.004960	-4.4	0.005173	-0.3
.7977	.006178	.005810	-6.0	.006234	+0.9
.6989	.007247	.006778	-6.4	.007419	+2.4
.5998	.008478	.007909	-6.8	.008736	+3.1
.5044	.009851	.009177	-6.8	.01014	+3.0
.3973	.01157	.01074	-7.1	.01190	+2.9
.3131	.01292	.01236	-4.3	.01341	+3.7
.2088	.01514	.01455	-3.9	.01545	+2.0
.1216	.01704	.01667	-2.2	.01731	+1.5
0.0000	.02014	.....	....	.....	....

This system is ideal as is evident from density, lack of change of volume, or heat evolved during mixing.

SERIES E. MIXTURES OF ETHYL BENZOATE AND BENZYL BENZOATE.

Molar fraction of ethyl benzoate.	$\eta$ (Exp)	Log. visc.	Diff. %	Cube root	Diff. %
1.0000	0.02014	.....	....	.....	....
.8963	.02371	0.02339	-1.4	0.02426	+2.5
.8023	.02749	.02678	-2.5	.02845	+3.5
.6906	.03249	.03146	-3.2	.03402	+4.7
.5941	.03740	.03616	-3.3	.03938	+5.2
.5054	.04309	.04109	-4.6	.04478	+3.9
.3945	.04948	.04821	-2.6	.05219	+5.4
.2973	.05695	.05546	-2.6	.05933	+4.2
.2475	.06108	.05960	-2.4	.06323	+3.5
.1549	.06898	.06825	-1.1	.07091	+2.8
.0465	.08039	.07961	-1.0	.08068	+0.4
0.0000	.08514	.....	....	.....	....

This system is ideal. There were no changes of volume or evolution of heat on admixture. It indicates that the two formulae have about the same deviation and are of equal value in predicting the facts.

SERIES F. MIXTURES OF ETHYL ACETATE AND BENZYL  
BENZOATE.

Molar fraction of ethyl acetate.	$\eta$ (Exp)	Log. visc.	Diff. %	Cube root	Diff. %
1.0000	0.004239	.....	....	.....	....
.8980	.006406	0.005756	-10.1	0.006876	+ 7.4
.7990	.009116	.007746	-15.0	.01032	+13.2
.6973	.01275	.01051	-17.5	.01489	+16.5
.5863	.01789	.01467	-18.0	.02122	+18.7
.5000	.02299	.01900	-17.3	.02724	+19.0
.4001	.03047	.02570	-15.6	.03536	+16.0
.3002	.03881	.03460	-10.9	.04528	+16.8
.2347	.04711	.04210	-10.7	.05258	+11.6
.1426	.05938	.05520	- 7.0	.06412	+ 8.0
.0784	.07003	.06728	- 4.0	.07307	+ 4.3
0.0000	.08514	.....	....	.....	....

This system is ideal as indicated by measurements of volume change, heat evolution, and depression of the freezing point of benzyl benzoate in each mixture of the two components. This system is also the most important of all. There was a wider range of viscosities of components than in any other system ever investigated. The viscosity of benzyl benzoate is nearly twenty times that of ethyl acetate; there is a difference of molecular weights of about 124. It is a very good system by which to detect the effects of factors that have as yet not been sufficiently studied.

The value of the viscosity of any mixture based on the logarithmic formula is about as near to the experimental data as that based on the cube root formula. The advantage of one formula over the other is not apparent.

Figure number two shows the curves of the values for each system. In each case, the values calculated from the logarithmic formula are less than the experimental data, while those of the cube root are greater. Only where there is a very large difference in the molecular weights of the components is there such a large variation in the experimental and calculated values as is shown in the ethyl acetate benzyl benzoate and the ethyl ether diphenyl ether systems.

That these experimental data lie between the values obtainable by the two formulae (logarithmic and cube root), is more apparent when we notice a summary of it.

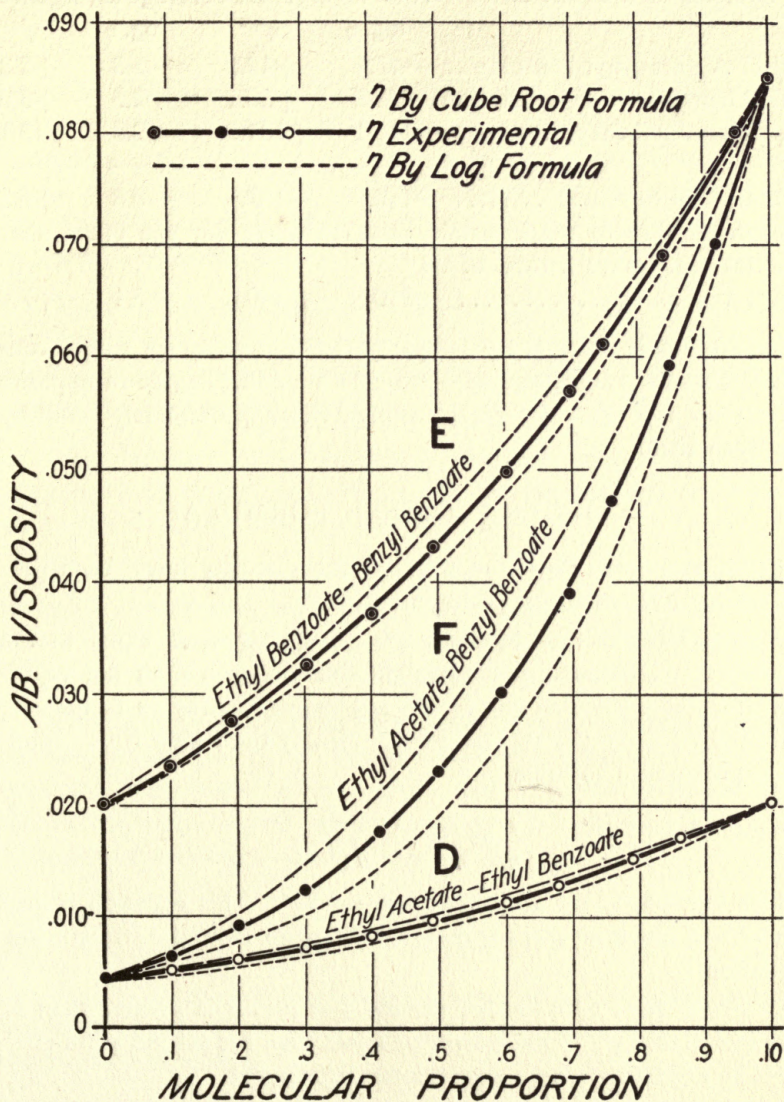


Fig. No. 2

## RESUME OF THE EXPERIMENTAL DATA

Systems of the Esters.	Total divergence.		Average divergence	
	log. $\eta$	$\eta^{1/3}$	log. $\eta$	$\eta^{1/3}$
ethyl acetate-ethyl benzoate ..	-47.9	+19.5	-5.3	+2.2
ethyl benzoate-benzyl benzoate	-24.7	+36.1	-2.5	+3.6
ethyl acetate-benzyl benzoate	-126.1	+131.5	-12.6	+13.1
Total— 29 mixtures .....	-198.7	+187.1	-6.8	+6.3
When we add to these results those obtained for the ether-ether mixtures, we have a total of 62 mixtures ..	-310	+490.6	-5.1	+7.9

From this summary of the experimental data, we would conclude that the two formulae deviate to a similar degree in opposite directions and that the ideal formula lies approximately midway between them.

## 9. OTHER POSSIBLE FORMULAE

Other powers than the third of the viscosity have been proposed for new empirical formulae.

The straight line equation  $\eta = x\eta_1 + (1-x)\eta_2$  is equal to the statement  $d\eta/dx = K$ . This straight line equation does not represent the facts since all the curves sag in such a way as to indicate that the viscosity ( $\eta$ ) increases more rapidly the bigger it is. Bingham proposed a formula

$$\frac{1}{\eta} = \frac{x}{\eta_1} + \frac{(1-x)}{\eta_2} \quad ^{24}$$

which is equal to the statement  $d\eta/dx = K\eta^2$ . This equation is also never true but it errs in the opposite direction from the straight line equation.

From these two we can deduce that  $d\eta/dx$  is greater than  $K$  but less than  $K\eta^2$ . Some power of  $\eta$  less than the second will therefore be expected to give approximate agreement.

By the logarithmic formula,

$$\text{Log } \eta = x \text{ log } \eta_1 + (1-x) \text{ log } \eta_2,$$

<sup>24</sup>See Bingham, Amer. Chem. Jour. 34, 481 (1905), Phys. Rev. 35 407 (1912).



which is equivalent to  $d\eta/dx=K\eta$ , we get values a little *less* than those of the experimental data and by the cube root equation

$$\eta=x\eta_1+(1-x)\eta_2,$$

which is equivalent to  $d\eta/dx=K\eta^{4/3}$ , we get values always *greater* than the facts, and can conclude that some equation with a power more than one and less than  $4/3$  will give an approximate agreement. Some such equation could be devised, but, as present, without some theoretical foundation, it would be but another empirical equation of doubtful value.

There is still the problem of accounting for the variations in the systems between the experimental data and that calculated upon the logarithmic formula whether this has a power of one or something between one and four-thirds.

This variation runs from about one per cent in systems of components of similar molecular weight, to ten per cent in systems where the molecular weights are far apart.

Here some factor, due to a change in molecular strain with change in composition, must operate to bring about the above noted differences in experimental and calculated values, which change with the wider range in viscosity of the components.

This change in molecular strain may be due to a change in the internal pressure or in the average molecular volume of the components. This latter factor accords well with the observed fact that the difference noted between experimental and calculated data increases with increase of molecular weight.

## 10. SUMMARY

Results obtained in the foregoing paper on the viscosity of ideal binary mixtures of the same class of components may be briefly summarized as follows:

1. Two sets of new data of high degree of accuracy have been obtained for mixtures whose components show wide range of variation of viscosity.

2. All formulae for ideal mixtures have been eliminated except the Arrhenius-Kendall logarithmic viscosity and the cube root

viscosity-molecular composition one of Kendall and Monroe. These formulae are shown to have nearly equal value. The equation for the ideal binary mixture must lie about midway between these two formulae.

3. The variations between the calculated and experimental viscosities are shown to be affected by some factor as yet not determined.

*VITA.*

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