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THE VISCOSITY OF LIQUIDS. II. THE VISCOSITY-COMPOSITION CURVE FOR IDEAL LIQUID MIXTURES.<sup>1</sup>

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The present unsatisfactory state of our knowledge of viscosity is universally admitted; there is scarcely a field in physical chemistry where more work has been done and less progress made. Dunstan and Thole<sup>2</sup> in their recent monograph introduce the subject thus: "In spite of a century of experimental work no definite method has been set up for the measurement of viscosity, and no general agreement has been arrived at for the setting forth and interpretation of the results obtained"—a statement commended by Bingham<sup>3</sup> in reviewing the volume.

Since the above monograph was written, the experimental difficulties therein discussed have practically disappeared, for we have in the apparatus devised by Bingham<sup>4</sup> a means of determining viscosity to a much

<sup>1</sup> For the first article in this series see Kendall, *Medd. K. Vetenskapsakad. Nobel-inst.*, **2**, No. 25 (1913).

<sup>2</sup> Dunstan and Thole, "The Viscosity of Liquids," Longmans, Green & Co. (1913).

<sup>3</sup> Bingham, *THIS JOURNAL*, **36**, 1320 (1914).

<sup>4</sup> Bingham, *J. Ind. Eng. Chem.*, **6**, 233 (1914); Bingham, Schlesinger and Coleman, *THIS JOURNAL*, **38**, 27 (1916). A somewhat similar type of apparatus has also been described by Washburn and Williams, *Ibid.*, **35**, 737 (1913).

higher degree of precision than with the old Ostwald type of viscometer. No corresponding theoretical advances have occurred, however; and from the failure of all attempts, under our existing knowledge, to derive from first principles general viscosity equations in agreement with the experimental facts, it appears that a successful *theoretical* attack can be made only when we have established an exact and comprehensive kinetic-molecular theory of liquids. The present route to progress is, therefore, necessarily experimental.

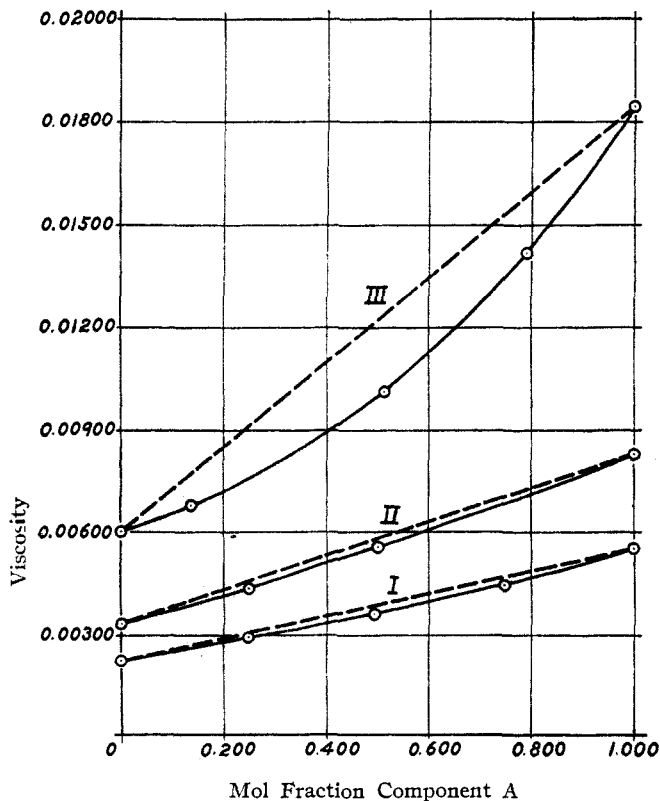


Fig. 1.

I. Toluene—ethyl ether, 25°. II. Decane—hexane, 25°. III. Nitrobenzene—benzene, 25°.

Our total ignorance regarding viscosity relationships is illustrated by a consideration of the viscosity-composition curves of binary liquid mixtures. Fig. 1 shows the experimental results for three typical systems<sup>1</sup> with presumably normal components.<sup>2</sup> It is evident that the simple

<sup>1</sup> See respectively, Getman, *J. chim. phys.*, 4, 398 (1906); Bingham *et al.*, *Z. physik. Chem.*, 83, 641 (1913); Linebarger, *Amer. J. Sci.*, [4] 2, 331 (1896).

<sup>2</sup> In the present article only *normal* or *ideal* liquid mixtures are discussed. A

linear law of mixtures:  $d\eta/dx = k$ ; (where  $\eta$  = viscosity,  $x$  = composition of mixture,  $k$  = constant) is never exactly obeyed, the observed viscosities being uniformly *lower* than the mixture rule would indicate.<sup>1</sup> The greater the difference in the viscosities of the two components, the greater is the sag towards the composition axis.<sup>2</sup>

Viscosity itself is consequently not a simple additive property. What is the *real* "additive property" (in other words, what function of viscosity enters into the general equation for the ideal-mixture curve) is a problem of fundamental importance. A knowledge of the ideal formula would certainly lead us far towards clearer conceptions of the strict physical meaning of viscosity and the nature of the molecular forces existent in liquids.<sup>3</sup> It would also enable us to predict the viscosity of any normal mixture from those of its components—a point of considerable industrial interest in connection with the blending of oils. Furthermore, until the *ideal* equation is known, no advance at all is possible in the study of *non-ideal* solutions by the viscosity method—a field which has attracted a great deal of attention in recent years.<sup>4</sup> Findlay<sup>5</sup> and Denison<sup>6</sup> claim that the nature of the complexes present in such solutions may be established from the position of maximum divergence from the normal curve, but such a rule obviously remains useless so long as the normal curve is not defined. The current procedure of arbitrarily assuming that it is linear is quite contrary to the facts of experiment, and is, therefore, "bound to reveal inconsistencies, and in many cases to lead to fallacious conclusions."<sup>7</sup>

system is *ideal* if there are no changes of molecular state, *i. e.*, no association, dissociation or combination, on admixture of its components. (Findlay, "Osmotic Pressure," p. 30.) Complete miscibility is also a condition of ideality, and in this connection such factors as polarity and internal pressure must be considered. (Hildebrand, *THIS JOURNAL*, 38, 1453 (1916).)

<sup>1</sup> Compare Thorpe and Rodger, *J. Chem. Soc.*, 71, 374 (1897); Dunstan, *Ibid.*, 85, 819 (1904).

<sup>2</sup> This is true whether composition is expressed in volume, weight or molecular fractions. The sag is usually least evident in the last case, since viscosity increases, in general, with the molecular weight. The above diagram therefore presents the most favorable aspect of the linear viscosity formula.

<sup>3</sup> See Dunstan and Thole, "The Viscosity of Liquids," preface. Our present definition of viscosity does not distinguish between gases and liquids (see, however, Bingham, *THIS JOURNAL*, 36, 1393 (1914)). Even for the vastly simpler case of gaseous mixtures no simple equation has yet been derived (Schmitt, *Ann. Physik*, [4] 30, 393 (1909)).

<sup>4</sup> Dunstan and co-workers, *J. Chem. Soc.*, 85, 817 (1904); 95, 1556 (1909), (also many papers of intermediate date); Tsakalotos, *Bull. soc. chim.*, [4] 3, 234 (1908); Faust, *Z. physik. Chem.*, 79, 97 (1912); Kurnakov and Shemtschushni, *Ibid.*, 83, 481 (1913); Bramley, *J. Chem. Soc.*, 109, 10 and 434 (1916).

<sup>5</sup> Findlay, *Z. physik. Chem.*, 69, 203 (1909).

<sup>6</sup> Denison, *Trans. Faraday Soc.*, 8, 20 (1912).

<sup>7</sup> Dawson, *Ann. Reports Chem. Soc.*, 13, 17 (1916).

Many efforts have been made in the past to derive empirically, from analysis of the available experimental data, a general formula relating viscosity and composition in ideal liquid mixtures, but a satisfactory solution has yet to be obtained. The present investigation initiates another attempt to elucidate the problem. The results of previous work upon the subject may first be briefly presented, in order to make clear the method of attack.

### Previous Work.

(a) *Proposed Formulae*.—The failure of the simple equation:

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

(where  $\eta_1$  and  $\eta_2$  are the viscosities of the pure components,  $x$  and  $(1 - x)$  the fractions of each in the mixture) has already been indicated.<sup>1</sup>

Lees,<sup>2</sup> from hydrodynamic theory, and Bingham,<sup>3</sup> from analogy between viscous and electrical resistance, have developed the formula

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

in which volume-composition units are employed. Under the hypotheses advanced by these workers, *fluidity* (the reciprocal of viscosity) is the truly additive property. Drucker and Kassel<sup>4</sup> have recently advocated the same equation with weight-composition units.

A different type of formula was proposed by Arrhenius<sup>5</sup> as early as 1887:

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

composition being again expressed in volume units. This equation may be written in the form

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

whence it appears that  $\log \eta$  is here considered as an additive function.<sup>6</sup> It is significant that Dunstan and Thole, in their extensive researches on the viscosities of homologous series of liquids,<sup>7</sup> find the same expression additive throughout.

Kendall<sup>8</sup> first pointed out that, since "viscosity is essentially the fractional resistance encountered by molecules of a solution in moving over one another,"<sup>9</sup> it would seem to be more logical to represent compositions in molecular, rather than in weight or volume fractions. The Arrhenius

<sup>1</sup> Composition fractions, in this formula, have been expressed by different investigators sometimes in volume and sometimes in weight units, no justification being given for either procedure.

<sup>2</sup> Lees, *Phil. Mag.*, [6] 1, 128 (1901).

<sup>3</sup> Bingham, *Amer. Chem. J.*, 34, 481 (1905); *Phys. Rev.*, 35, 407 (1912).

<sup>4</sup> Drucker and Kassel, *Z. physik. Chem.*, 76, 367 (1911).

<sup>5</sup> Arrhenius, *Ibid.*, 1, 285 (1887).

<sup>6</sup> The above formula is simultaneously a logarithmic viscosity and a logarithmic fluidity equation, since  $\log \eta = -\log (1/\eta)$ .

<sup>7</sup> Dunstan and Thole, "The Viscosity of Liquids," pp. 32-38.

<sup>8</sup> Kendall, *Medd. K. Vetenskapsakad. Nobelinst.*, 2, No. 25 (1913).

<sup>9</sup> Noyes, *THIS JOURNAL*, 34, 457 (1912).

equation, when so modified, was found to fall into much closer agreement with the then available experimental results.<sup>1</sup>

Equations of greater complexity (such as those in which an additional constant is introduced)<sup>2</sup> need not be discussed here. The constants added are always purely arbitrary, and while such formulas are occasionally useful for interpolation purposes, they can never be invested with any theoretical significance.

(b) *Comparison with Experimental Data.*—Little accurate experimental work has been done upon systems of normal type, the energies of investigators having been occupied almost exclusively in the examination of curves which diverge so much from the normal as to exhibit maxima or minima. In such systems it is recognized that considerable interaction between the two components has taken place.<sup>3</sup> A minimum is considered to indicate the dissociation of an associated liquid (*e. g.*, acetone-carbon bisulfide), a maximum to indicate the formation of addition compounds (*e. g.*, acetic acid-aniline).<sup>4</sup>

It will be evident that a *general* viscosity equation can be applicable only to *normal* systems, and cannot include mixtures in which any changes of molecular state occur. It must also be noted, however, that even where the curve appears to exhibit the normal type (see Fig. 1), molecular changes may have taken place on admixture which are insufficient to induce a maximum or a minimum.<sup>5</sup> A careful selection of systems is, therefore, necessary.

A number of systems containing *presumably* non-associated and chemically indifferent liquids have been examined by Thorpe and Rodger,<sup>6</sup> Linebarger,<sup>7</sup> Dunstan,<sup>8</sup> Getman,<sup>9</sup> and Bingham.<sup>10</sup> It is of interest to com-

<sup>1</sup> Arrhenius has recently shown that the same formula is also applicable to suspensions of colloids. See *Medd. K. Vetenskapsakad. Nobelinst.*, 3, No. 13 (1916).

<sup>2</sup> See Lees, *Loc. cit.*; Sakhanof and Ryaklofski, *J. Russ. Phys. Chem. Soc.*, 47, 113 (1915).

<sup>3</sup> It is of interest to note here the general similarity between viscosity-composition curves and vapor pressure-composition curves. Both are of three general types, and for the two *abnormal* types the same explanation is adduced. The connection may be carried further and may possibly have fundamental significance. Bingham has shown (*Amer. Chem. J.*, 47, 185 (1912)) that liquids in the same homologous series possess equal viscosities at temperatures of *identical* vapor pressure. The analogy fails only at one point (unfortunately the most important)—the ideal-mixture curve, which for viscosity is certainly not linear, even when expressed in molecular composition units (see Fig. 1).

<sup>4</sup> Faust, *Z. physik. Chem.*, 79, 97 (1912). This paper also includes a valuable list of references.

<sup>5</sup> Bingham, *J. Phys. Chem.*, 18, 157 (1914).

<sup>6</sup> Thorpe and Rodger, *J. Chem. Soc.*, 71, 360 (1897).

<sup>7</sup> Linebarger, *Amer. J. Sci.*, [4] 2, 331 (1896).

<sup>8</sup> Dunstan and Stubbs, *J. Chem. Soc.*, 93, 1919 (1908).

<sup>9</sup> Getman, *J. chim. phys.*, 4, 398 (1906).

<sup>10</sup> Bingham, *Z. physik. Chem.*, 83, 641 (1913).

pare the agreement of the various equations given above with their combined data. The results for a total of 84 mixtures are summarized in the following table. The *average* divergences between calculated and observed values are given in the first column, the *maximum* divergences (with the sign indicated) in the second, and the *directional* divergences (*i. e.*, the excess of divergences of one sign over those of opposite sign, averaged for all the mixtures) in the third.

Formula.	Average divergence.	Maximum divergence.	Directional divergence.
Viscosity—volume composition.....	11.1%	+66%	+10.2%
Log. Viscosity—volume composition.....	4.7	+27	+ 3.6
Fluidity—volume composition.....	3.4	-22	- 1.8
Fluidity—weight composition.....	3.2	-15	- 0.1
Log. Viscosity—molecular composition.....	2.3	+ 8	+ 0.2

It will be seen that the average divergences are small, except for the first two formulas, which almost invariably give calculated values far too high. In the third equation, the calculated values are generally somewhat low; with regard to the two last equations it is hard to draw any definite conclusions from the above table. The errors of experiment are greatly exceeded in almost all cases, but the divergences are sometimes positive and sometimes negative, and may quite conceivably be due entirely to non-ideality of the solutions.<sup>1</sup> Measurements of heat effects and volume changes on admixture have seldom been carried out for these particular systems, and we have no assurance that any of the mixtures examined are truly normal. Even with commonly assumed "indifferent liquids," small changes of temperature and of volume often accompany admixture, and viscosity is such an exceedingly sensitive property that relatively large divergences from the normal curve may thus be occasioned.<sup>2</sup>

Deviations of the magnitude given above are, therefore, insufficient to warrant the final rejection of any formula. The question of the true ideal-mixture equation is left quite undecided, since not only may any of the above be valid, but also further alternative formulas (such as fluidity-molecular composition, etc.) cannot be denied possible titles to consideration.

<sup>1</sup> This important point has been discussed in detail by Bingham, *J. phys. Chem.*, 18, 157 (1914). One error in this paper, however (page 161) must be pointed out here. The hypothesis that fluidity is an additive property is *not* placed at any disadvantage by taking viscosity curves which show neither maximum nor minimum as material for comparison in the table above. If fluidity curves without maximum or minimum were taken as normal the result would necessarily be *the same*, since a maximum in  $\eta$  means a minimum in  $1/\eta$ , and *vice versa*. The case is therefore not prejudged in the slightest degree by the choice of data.

<sup>2</sup> The case of ethyl acetate and nitrobenzene (Linebarger, *Loc. cit.*) may be instanced. Here there is a contraction of 0.8% for an equi-volume mixture, and the viscosity is much greater than normal.

The present investigation obtains a decision between the various claimants by the simple expedient of extending the experimental range.

### Experimental.

Previous workers have restricted their measurements to systems such as benzene-toluene, chloroform-carbon tetrachloride, where the viscosities, densities and molecular weights of the pure components are not widely separated.<sup>1</sup> In such a case, no equation is permitted much opportunity to escape very far from the experimental curve, and still less to distinguish itself clearly from the other equations. In spite of what has been said above regarding non-ideality, therefore, agreement with the experimental data is here, after all, more a matter of necessity than of merit, and, however faithfully a particular formula may follow the observed values for any one system, the other calculated curves are, in general, so closely clustered about it that no real discrimination is feasible.<sup>2</sup>

The systems here investigated have been specially selected to obviate such confusion. The components of each mixture, besides being as nearly as possible ideal, differ widely both in viscosity and in molecular weight.<sup>3</sup> The consequence is that all of the nine curves obtained by plotting viscosity, fluidity or logarithmic viscosity against volume, weight or molecular composition diverge considerably from one another, and a comparison of their claims to represent the experimental data can readily be made.<sup>4</sup>

For the experimental work, the accurate apparatus devised by Bingham<sup>5</sup> was employed and his methods of measurement were substantially followed.

A low-pressure reservoir was connected to viscometer, water-manometer and filter-pump. Constant pressure was ensured throughout an experiment by careful adjustment of an additional stopcock leading from the reservoir, with a pin-hole outlet to the atmosphere. Water levels in the manometer were read on a fixed steel tape backed by a plate-glass mirror. The viscometer was clamped vertically in a well-insulated glass thermostat, regulated electrically to a standardized temperature of  $25 \pm 0.02^\circ$ .

Every reasonable precaution was taken to keep all apparatus clean and dust-free. After each measurement the viscometer was treated with

<sup>1</sup> In the whole series of mixtures examined above, the viscosities of the two components are never in a greater ratio than 4 to 1. Rarely, indeed, is the ratio as high as 2 to 1.

<sup>2</sup> Thus in the system benzene-toluene (Linebarger, *Loc. cit.*) the maximum divergence between the ten different equations considered below is only 3%.

<sup>3</sup> Density differences are more difficult to establish; see however Fig. 2, where volume and weight equations are clearly distinguished.

<sup>4</sup> Some idea of the effect of even a small increase in the viscosity-ratio upon the form of the experimental curve and its relation to the linear viscosity formula may be gained by contrasting Curve III with Curves I and II in Fig. 1.

<sup>5</sup> Bingham, *J. Ind. Eng. Chem.*, 6, 233 (1914).

chromic acid mixture, rinsed thoroughly with freshly distilled water,<sup>1</sup> and dried by a prolonged current of filtered air. The flasks and pipets employed in the preparation of solutions, also the pycnometers used in the determination of densities,<sup>2</sup> were similarly treated.

Solutions were made up by weighing the required amounts of the two components into a 50-cc. glass-stoppered flask; after thorough shaking, the necessary volume of the mixture was pipeted into the viscometer. This was immediately attached to the low-pressure reservoir, and exact adjustment of the working volume made. The time of flow between the two fixed marks was then observed, duplicate measurements in reverse directions being taken several times for each mixture. The pressures employed were varied in different systems, so that the time of flow was never shorter than 4 minutes.<sup>3</sup>

The experimental error of the method is less than 0.1%, as may be seen from the following typical series: ( $p$  = pressure in g. per sq. cm.;  $t$  = time of flow in secs. For approximately constant values of  $p$ ,  $pt$  should be a true constant.)

TABLE I.—WATER AT 25° IN VISCOMETER I.

(a) Empty.			(b) Fill.		
$p$ .	$t$ .	$pt$ .	$p$ .	$t$ .	$pt$ .
95.11	403.2	38348	95.21	403.3	38398
95.19	403.4	38400	95.21	403.2	38388
95.14	403.2	38360	95.22	403.1	38384
95.12	402.9	38324	95.23	403.2	38397
95.22	403.0	38375	95.15	403.3	38375
Mean, 38361			Mean, 38388		

**Standardization of Apparatus.**—The viscometers employed were standardized by means of water at 25°, for the viscosity of which the absolute value  $\eta = 0.008946$  was taken.<sup>4</sup> For any given instrument the complete viscosity formula<sup>5</sup>

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

<sup>1</sup> The laboratory "distilled water" was purified by distilling first over alkaline permanganate and later alone.

<sup>2</sup> Accurate densities were needed in this investigation only to transpose mixtures from weight to volume composition units. The viscosity method employed (see below) does not, in itself, call for more than approximate density determinations.

<sup>3</sup> The stop-watch used was of best Swiss make and could be read to 0.1 sec. Its accuracy was tested at intervals by an expert horologist.

<sup>4</sup> This value was communicated to us by Prof. Bingham as the most probable result indicated by the determinations of Poiseuille, Sprung, Slotte, Thorpe and Rodger, Hosking, and Bingham and White. See *Z. physik. Chem.*, **80**, 685 (1912).

<sup>5</sup> Dunstan and Thole, "The Viscosity of Liquids," p. 2; Bingham and White, *Loc. cit.*, pp. 681-3.



( $g$  = acceleration due to gravitation;  $r$  = radius of capillary;  $v$  = transpiration volume;  $l$  = length of capillary;  $n$  = number of capillaries;  $\rho$  = density of liquid), reduces to the form

$$\eta = Cpt - C'/\rho t.$$

Since the second term (the kinetic energy correction) is of comparatively small importance,<sup>1</sup>  $C'$ , which equals  $1.12nV/8\pi l$ , is obtained with sufficient accuracy by direct approximate measurement. The value of  $C$  may then be readily established from experiments with a standard liquid.

Bingham, Schlesinger and Coleman<sup>2</sup> have recently shown that a slight modification of the working formula is necessary to ensure constant values for  $C$  under different pressures. This is due to the fact that the *true* average pressure  $p$ , driving the liquid through the viscometer, is not equal to the *observed* manometer pressure  $p_0$ , but is given by the relation

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

(where  $h$  is the maximum head of liquid in the viscometer). The significance of the correction thus involved<sup>3</sup> is evident from the following table:

TABLE II.—WATER IN VISCOMETER I AT 25°.

Manometer pressure.	C.	True average pressure.	C (corrected).
130.00	0.062565	129.71	0.062571
95.00	0.062560	94.63	0.062570
60.00	0.062546	59.43	0.062570

The viscometer constant is thus established within the error of experiment (see Table I, p. 1794). That it did not vary during the course of the investigations was verified by testing at intervals; the last determination with Viscometer I (after more than 30 mixtures had been examined) gave a value of 0.062569.

The consistency of the final viscosity values obtained for a pure liquid may be indicated by the following results for four different preparations of benzene:

$$\eta_{25} = 0.006044; 0.006051; 0.006048; 0.006051. \quad \text{Average, } 0.006049.^4$$

For binary solutions the results do not quite reach this order of accuracy, although the source of error here lies not so much in the viscosity measurements as in the exact determination of percentage compositions.<sup>5</sup> Differential evaporation of the two components during an experiment cannot be entirely avoided. The free space, however, is small throughout, and

<sup>1</sup> In the present series of measurements it never exceeded 1.5% of the total value.

<sup>2</sup> Bingham, Schlesinger and Coleman, *THIS JOURNAL*, 38, 27 (1916).

<sup>3</sup> This correction amounted at most, under the pressures employed, to 1.5%.

<sup>4</sup> Getman, *J. chim. phys.*, 4, 398 (1906) obtained the value 0.00606, but other values recorded by previous investigators show wide divergences.

<sup>5</sup> Compare Kendall, *J. Chem. Soc.*, 101, 1282 (1912).

it is believed that this error does not exceed 0.2% in the most unfavorable cases, while in most mixtures its effect is certainly inappreciable.<sup>1</sup>

The results for one system are examined in detail below. The remaining systems, which are all precisely similar in nature, are subsequently more briefly presented.

#### The System: Benzene-Benzyl Benzoate.<sup>2</sup>

So far as can be judged, this system is ideal.<sup>3</sup> Careful calorimetric measurements failed to indicate any heat evolution or absorption on admixture of equal volumes of the two liquids.<sup>4</sup> Density determinations showed that no volume change occurred. The freezing point of benzene was found to be normally depressed on addition of benzyl benzoate, just as with other esters.<sup>5</sup> The polar natures and internal pressures<sup>6</sup> of the two liquids are substantially similar.

We have here extremely favorable conditions for deciding between the various possible formulas for the ideal curve. The viscosity of benzyl benzoate is 14 times that of benzene, its molecular weight is almost 3 times as large, its density nearly 30% higher. The effect of these factors in scattering the different equations may be seen from the following tables, and also from the annexed diagram (Fig. 2).

The first column in each table indicates the composition of the mixtures, the second their observed viscosity, the remaining columns the percentage errors in the viscosities calculated according to each mixture formula. The significance of the "cube root equation" in the last column of Table IIIc will be discussed below.

It will be evident from these tables that, whatever the composition units selected, none of the equations tested is in even remote agreement with experimental facts. With viscosity formulas the maximum deviations are from 204 to 74%, with fluidity formulas from 63 to 36%, with log. viscosity formulas from 48 to 27%.

<sup>1</sup> Where the more volatile liquid is in excess, a relatively large weight must be removed by evaporation to produce a noticeable effect on viscosity (see Curve I, Fig. 2); where its molecular fraction is small, its volatility is correspondingly reduced.

<sup>2</sup> Crystallized, thiophene-free benzene was dried over sodium and fractionated. The fraction accepted boiled at 80.2–80.3° (corr.), and froze at 5.480° (compare Young, "Fractional Distillation," p. 116; Richards and Barry, *THIS JOURNAL*, **37**, 993 (1915)). Benzyl benzoate was fractionated under reduced pressure; the fraction employed gave a m. p. 18.8° (compare Kendall and Booge, *THIS JOURNAL*, **38**, 1721 (1916)).

<sup>3</sup> No system, of course, can be absolutely ideal; even two saturated hydrocarbons will not be altogether indifferent to each other. The tests made above, however, are sufficient to establish the fact that any abnormality is here inappreciable.

<sup>4</sup> Kremann, *Monatsh.*, **37**, 369 (1916) has recently stated that the mixing of normal liquids is accompanied by heat absorption. How this can be true it is difficult to conceive. Two portions of the same liquid are certainly ideal with respect to one another, yet no one would expect heat absorption to result from their admixture!

<sup>5</sup> Unpublished work by Dr. J. E. Booge.

<sup>6</sup> Hildebrand, *THIS JOURNAL*, **38**, 1459 (1916).

TABLE III (a).—BENZENE-BENZYL BENZOATE. WEIGHT-COMPOSITION EQUATIONS.

Wt. % ester in mixture.	$\eta$ (Expt.).	Percentage divergence.		
		Viscosity eqn.	Fluidity eqn.	Log. visc. eqn.
0.00	0.006044	..	..	..
38.71	0.01196	+204	-21.1	+39.5
65.60	0.02301	+150	-32.8	+48.3
79.17	0.03584	+90.2	-36.3	+36.2
90.73	0.05478	+41.1	-29.9	+30.5
95.88	0.06883	+21.3	-19.9	+10.1
100.00	0.08454	..	..	..

TABLE III (b).—BENZENE-BENZYL BENZOATE. VOLUME-COMPOSITION EQUATIONS.

Vol. % ester in mixture.	$\eta$ (Expt.).	Percentage divergences.		
		Viscosity eqn.	Fluidity eqn.	Log. visc. eqn.
0.00	0.006044	..	..	..
33.08	0.01196	+168	-21.0	+27.0
59.91	0.02301	+131	-40.8	+27.6
74.84	0.03584	+80.8	-44.7	+21.4
88.44	0.05478	+37.8	-38.3	+13.7
94.78	0.06883	+21.0	-26.9	+7.0
100.00	0.08454	..	..	..

TABLE III (c).—BENZENE-BENZYL BENZOATE. MOLECULAR-COMPOSITION EQUATIONS.

Mol. % ester in mixture.	$\eta$ (Expt.).	Percentage divergences.			
		Visc. eqn.	Fluid. eqn.	Log. visc. eqn.	Cube root eqn.
0.00	0.006044	..	..	..	..
18.86	0.01196	+74.2	-38.7	-17.0	+2.6
41.24	0.02301	+66.9	-57.5	-27.0	+3.8
58.32	0.03584	+44.6	-63.2	-21.5	+2.0
78.27	0.05478	+23.2	-59.6	-13.0	+2.7
89.52	0.06883	+10.9	-48.0	-6.8	+1.6
100.00	0.08454	..	..	..	..

Fig. 2 expresses the same results graphically. Viscosity is plotted against percentage composition; Curve A shows the viscosity equation, Curve B the fluidity, Curve C the log. viscosity. The experimental results are represented under weight, volume, and molecular composition units by the full Curves I, II and III, respectively. In no case is there any suggestion of accordance with any of the proposed formulas.

Now it is certain that the system does not deviate from the normal to any such extent as is here indicated. The nature of the results obtained consequently forces us to suspect that *none* of the equations considered has any claim to be regarded as the correct ideal-mixture formula. This suspicion is amply confirmed by an examination of the remaining systems investigated below. In no single instance is there even approximate agreement with any of the nine equations tested. The experimental curve uniformly falls exactly as in Diagram II, the log. viscosity-molecular composition curve being least distant from it, but the divergences even

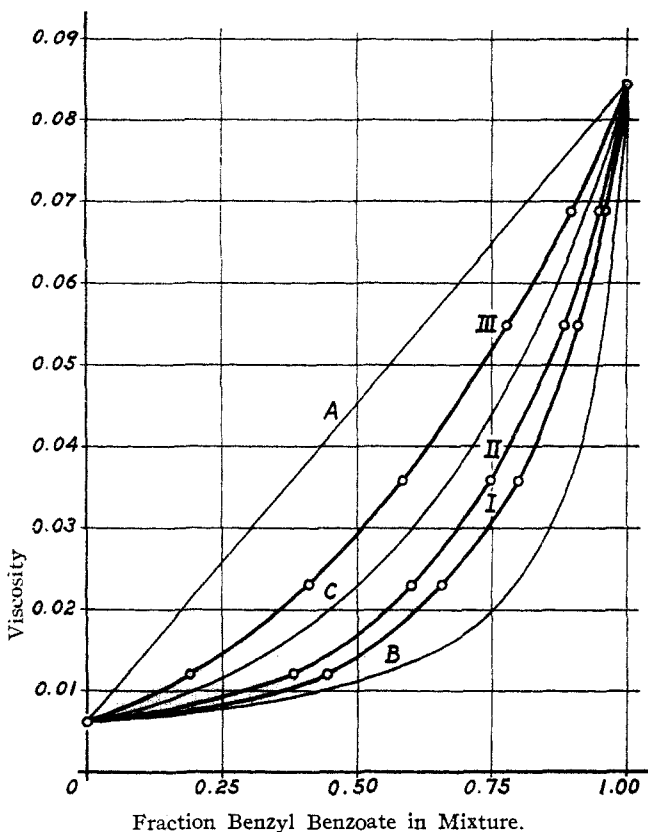


Fig. 2.

Calculated curves:	Experimental curves:
A = linear viscosity.	I = weight composition.
B = linear fluidity.	II = volume composition.
C = logarithmic viscosity (or fluidity).	III = molecular composition.

for this formula being far beyond any possible non-ideality of the mixtures.

We are, therefore, left with a clear field in which to begin anew our search for the true ideal-mixture equation. Out of a large number of expressions considered, the following only was found to afford satisfactory results:

$$\eta^{1/2} = x\eta_1^{1/2} + (1-x)\eta_2^{1/2}$$

Compositions are here represented in molecular units, and  $\eta^{1/2}$  is regarded as an additive function.<sup>1</sup> The agreement of this equation with the experi-

<sup>1</sup> It may be noted that the employment of the function  $\eta^{1/2}$  is not merely the result of a "wild guess," for the function does possess a possible fundamental significance. Batschinski (*Bull. soc. imp. nat. Moscow*, 1901, 1) has shown that the equation

mental data may be seen from the last column in Table IIIc. The maximum divergence is only 3.8%; this is still far in excess of errors of measurement, but may quite conceivably be due to non-ideality. In Fig. 2 the curve derived from the above equation runs so closely beside the observed Curve III throughout the whole composition range that it is impossible to indicate it without confusing the diagram.

The question now arises: Is the success of the "cube root formula" in this particular instance due entirely to chance, or is the formula really capable of representing binary ideal mixtures in general? The answer may be sought by testing the equation immediately against the other systems here studied.

#### The System: Benzene-Ethyl Benzoate.<sup>1</sup>

This mixture has been previously investigated by Linebarger<sup>2</sup> with a viscometer of the Ostwald type. That the system is substantially normal was established by the usual calorimetric and volumetric tests.

The results obtained are given in Table IV, p. 1800.<sup>3</sup> The first three columns indicate the compositions of the mixtures examined, in weight, volume and molecular units, respectively. The fourth column shows the observed viscosities, the fifth the viscosities calculated from the cube root formula, the sixth the percentage differences between these values.

$\eta^{1/3}T = k$  represents the variation of viscosity with absolute temperature for many pure liquids with approximate accuracy. It is true that the same author has more recently (*Z. physik. Chem.*, **84**, 644 (1913)) proposed a fluidity-volume formula which expresses this variation more closely, but the increased concordance is here due more to the introduction of a second arbitrary constant than to any true superiority. This fluidity-volume equation is found, on close examination, to be purely an interpolation formula, valid over the relatively small temperature ranges considered, but breaking down completely at higher or lower temperatures. It cannot therefore be considered to witness in favor of fluidity as an additive function (see Bingham, *J. phys. Chem.*, **18**, 163 (1914)). Indeed, it is not difficult to derive other two-constant equations which are still more concordant with the experimental data over the same temperature intervals. The formula  $\log \eta^{1/3} = a/T + b$  may be cited. Further discussion of this point, however, lies beyond the scope of the present paper.

<sup>1</sup> Ethyl benzoate was fractionated under reduced pressure. The fraction accepted gave a corrected m. p. of  $-32.3^\circ$ . (Compare Kendall and Booge, *THIS JOURNAL*, **38**, 1720 (1916).)

<sup>2</sup> Linebarger, *Loc. cit.* The viscosities found by Linebarger are consistently lower than those here recorded. The error may be one of apparatus, since the kinetic energy correction with the Ostwald instrument is always uncertain. In the present system all likely impurities (*e. g.*, toluene in benzene, ethyl alcohol in ethyl benzoate) would tend to *lower* the observed viscosity, thus furnishing another possible explanation of the discrepancy.

<sup>3</sup> In order to economize space in this and subsequent tables, the divergences of all the equations previously proposed are not presented in detail as in Table III above. The failure of all these formulas can readily be appreciated by plotting the curves with the use of the composition data here shown.

TABLE IV.—BENZENE-ETHYL BENZOATE.

Per cent. ester in mixture.			Viscosity.		Percentage divergence.
(a) Weight.	(b) Volume.	(c) Molecular.	Experimental.	Calculated.	
0.00	0.00	0.00	0.006051	....	...
22.35	19.43	13.02	0.007244	0.007279	+0.5
54.19	49.78	38.08	0.01018	0.01008	-1.0
67.74	63.75	52.18	0.01200	0.01195	-0.4
75.14	71.70	61.11	0.01327	0.01323	-0.3
85.86	83.57	75.98	0.01557	0.01557	0.0
91.47	90.00	84.79	0.01709	0.01707	-0.1
100.00	100.00	100.00	0.01991	....	...

It will be seen that the agreement is exceedingly good throughout. The viscosity range of the mixture, however, is not nearly so large as in the previous case.

#### The System: Toluene-Ethyl Benzoate.<sup>1</sup>

This system has also been examined by Linebarger, whose results are again uniformly lower than those here obtained. No heat effect or volume change on admixture of equal volumes of the two liquids could be observed.

TABLE V.—TOLUENE-ETHYL BENZOATE.

Per cent. ester in mixture.			Viscosity.		Percentage divergence.
(a) Weight.	(b) Volume.	(c) Molecular.	Experimental.	Calculated.	
0.00	0.00	0.00	0.005520	....	...
22.67	19.51	15.24	0.006845	0.006979	+1.9
47.26	42.56	35.46	0.009076	0.009287	+2.3
73.51	69.64	62.99	0.01279	0.01316	+2.9
81.90	78.90	73.49	0.01452	0.01490	+2.6
89.85	87.98	84.42	0.01655	0.01684	+1.7
100.00	100.00	100.00	0.01990	....	...

Again the divergences between calculated and observed values are small throughout. Other formulas show considerable deviations.

#### The System: Toluene-Benzyl Benzoate.

We have no reason to believe that this system is in any way less normal than those already tested; no heat effect or volume change was obtained on admixture of the two liquids. Comparatively large divergences, however, exist between experimental and calculated results throughout the whole composition range, as may be seen from Table VI.

<sup>1</sup> Purest toluene was shaken with conc. sulfuric acid until the absence of coloration on standing showed that all olefines had been removed. It was then treated with excess of pure calcium oxide to remove sulfuric acid and water, filtered, and repeatedly fractionated. The fraction accepted boiled at  $110.56^\circ \pm 0.03^\circ$  (corr. to 760 mm. pressure). This is not in agreement with the value  $110.3^\circ$  obtained by Richards and Barry, *This Journal*, 37, 993 (1915). Dr. Barry (to whom we extend our thanks for collaboration in this purification) is at present investigating the cause of the divergence. It may be noted that the viscosities of different samples prepared were identical, and also in accordance with the value of Getman (*J. chim. phys.*, 4, 398 (1906)), 0.00553.

TABLE VI.—TOLUENE-BENZYL BENZOATE.

Per cent. ester in mixture.			Viscosity.		Percentage divergence.
(a) Weight.	(b) Volume.	(c) Molecular.	Experimental.	Calculated.	
0.00'	0.00	0.00	0.005520	...	..
41.69	35.58	23.67	0.01183	0.01362	+15.1
63.11	56.93	42.61	0.02015	0.02399	+19.1
81.09	76.82	65.02	0.03614	0.04182	+15.7
89.60	86.94	78.90	0.05080	0.05645	+11.1
95.41	94.16	90.02	0.06660	0.07024	+ 5.5
100.00	100.00	100.00	0.08450	...	..

These results were unexpected, and their exact meaning must remain uncertain until further work has been done on this field. Most probably it will be found that the cube-root formula, like those previously advanced, possesses no strict theoretical foundation. It is less likely that any formula will reproduce the experimental curve merely by chance, the wider the difference between the viscosities of the two components of any system, and here the range is the greatest of any system examined. Consequently the utmost that can be claimed for the cube-root equation at the present time is that it approximates to the observed values much more closely than any other formula proposed. In fact, with most of the experimental data of previous workers (see p. 1791) the agreement is nearly perfect.<sup>1</sup>

We are continuing this investigation by taking up other mixtures with large viscosity differences. Only when a considerable number of such systems have been completed can the simple ideal-mixture equation (if any such really exists) be definitely established from the direct experimental results. It may be, of course, that the true equation is so exceedingly complex (other factors, such as internal pressure, average molecular volume,<sup>2</sup> etc., entering into consideration) that it can never be arrived at except theoretically. Even in that case, however, the data presented in these articles will prove of immediate service in verifying or disproving any such theoretical equation as soon as propounded.

#### Summary.

The viscosity curves of the following liquid systems, presumably ideal, have been determined by the experimental method of Bingham: (1) Benzene-benzyl benzoate; (2) benzene-ethyl benzoate; (3) toluene-ethyl benzoate; (4) toluene-benzyl benzoate.

Since the components of each mixture differ widely both in viscosity and in molecular weight, the results obtained render possible a decisive test between the various formulas which have been proposed to represent

<sup>1</sup> It is of interest to note that the cube-root formula is in much better agreement with the system hexane-decane, studied by Bingham (*Z. physik. Chem.*, **83**, 641 (1913)), than any other equation here examined. This mixture probably approaches the ideal as closely as any actual mixture studied.

<sup>2</sup> Tinker, *Phil. Mag.*, [6] **33**, 430 (1917).

such curves. Nine alternative linear functions have been considered—viscosity, fluidity and logarithmic viscosity, each being taken as an additive property against weight, volume and molecular composition units in turn.

It has been conclusively shown that none of these nine equations are even in approximate agreement with experimental facts. All must, therefore, be entirely devoid of theoretical significance.

A new empirical cube-root formula has been presented, which falls into much closer agreement with observed values. Only for the last system investigated are the divergences appreciable.

Further work is being carried on on similar ideal systems in order to obtain a more definite idea of the merits of this equation.

NEW YORK CITY.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY  
No. 305.]

### THE VISCOSITY OF LIQUIDS. III. IDEAL SOLUTIONS OF SOLIDS IN LIQUIDS.<sup>1</sup>

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It was hoped that a study of suitable systems of this type might solve the question left undecided at the close of the preceding paper, *i. e.*, whether the relative success of the cube-root viscosity equation there considered was due entirely to chance, or whether it might possess actual theoretical significance.

Previous work on the viscosities of ideal solutions of solids in liquids is extremely scanty.<sup>2</sup> Suggested formulas are, in general, similar in form to those for binary liquid mixtures, and similarly unsatisfactory in practice. Thus the linear equation

$$\eta = (1 + Ax)\eta_0$$

(where  $\eta_0$  = viscosity of pure solvent;  $x$  = weight of solute in unit volume of solution;  $A$  = constant) is valid only for very dilute solutions. The logarithmic equation of Arrhenius<sup>3</sup>

$$\eta = A^x \cdot \eta_0; \text{ or } \log(\eta/\eta_0) = x \log A$$

also becomes useless at higher concentrations. The fluidity formula of Lees<sup>4</sup>

$$1/\eta = x/\eta_0 + (1 - x)/\eta_1$$

regards the most concentrated solution as a second component with vis-

<sup>1</sup> Preceding articles; Kendall, *Medd. K. Vetenskapsakad. Nobelinstit.*, 2, No. 25 (1913), and Kendall and Monroe, *This Journal*, 39, 1787 (1917).

<sup>2</sup> See Dunstan and Thole, *J. Chem. Soc.*, 97, 1249 (1910).

<sup>3</sup> Arrhenius, *Z. physik. Chem.*, 1, 285 (1887).

<sup>4</sup> Lees, *Phil. Mag.*, [6] 1, 139 (1901).