THE VISCOSITY OF LIQUIDS ABOVE THEIR BOILING POINTS. PART I.

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Although numerous works on the viscosity of liquids have been published, very few of these researches are extended over a wide temperature range.(1) It was with the object of making up this deficiency that the writer undertook a series of determinations of viscosities of pure liquids above their boiling points. These experimental researches were followed by a study on the relation between viscosity of liquids and their volume and temperature.

Experimentals.

Preparation of Material. The materials used in this experiment are methyl-acetate, carbon-tetrachloride, fluorobenzene, chlorobenzene, and ethyl alcohol, of which the first four are usually regarded as normal liquids.

Methyl-acetate. A specimen from Merck was treated repeatedly with phosphorus pentoxide and finally fractionated. B.P. = 57.0°±0.01.

Carbon-tetrachloride. A pure specimen was obtained from Kahlbaum, which, being dehydrated over phosphorus pentoxide, boiled quite constantly. B.P. = 76.75°±0.00.

Fluorobenzene. This compound was prepared as described by Holleman and Beekman(2) by the action of concentrated hydrofluoric acid on benzenediazofluoride (C_6H_5.N.N.F.). Having been dried over calcium chloride, it was purified by fractional distillation. B.P. = 84°.8±0.05.

Chlorobenzene. A specimen from Kahlbaum was dehydrated over phosphorus pentoxide and purified by fractional distillation, until a product of quite constant boiling point was obtained. B.P. = 131°.74±0.01.

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(1) Stoel, Diss. Leiden, (1891); *Comm. Phys. Lab. Univ. Leiden*, 2 (1891); de Haas. ibid., 12 (1894); Warburg and v. Babo, *Wied. Ann.*, 17 (1882), 390; A. Heydweiller, *Wied. Ann.*, 55 (1895), 561; ibid., 59 (1896), 198; P. Phillips, *Proc. Roy. Soc. (London)*, (A) 87 (1912), 48

(2) Holleman and Beekman, *Rec. trav. chim.*, 23 (1905), 231; ibid., 24 (1905), 26.

Ethyl alcohol. Pure absolute alcohol from Merck was purified as described by Thorpe and Rodger⁽¹⁾ by distilling several times over freshly burnt quicklime. B.P. = 78°.27±0.02.

Description of Apparatus. At first several observations were made with methyl-acetate and fluorobenzene after the mercury-method described by A. Heydweiller.⁽²⁾ But as this method contains several difficulties and inaccuracy, a new apparatus was devised, by means of which the viscosities of the other three liquids were determined above their boiling points.

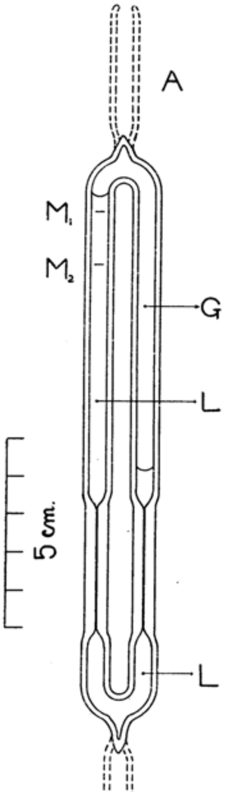

Fig. 1.

The appearance of the viscosimeter is shown in Fig. 1. Two parallel capillaries which have exactly equal inner diameter of 0.326 mm. and almost equal length (33 mm. and 32 mm.) are connected with each other by two U-tubes having uniform diameter of 4 mm. The total length of the upper U-part is 20 cm. and the lower 6 cm. The viscosimeter is cleaned by sucking successively hydrochloric acid, chromic acid, distilled water, alcohol and benzene and finally dry air through the annexed tube A or B (shown by dotted lines in the figure). Both limbs of the viscosimeter are so made as to exert equal resistance to the passing fluids.

It is then filled in the following manner: Having sealed the tube B, proper quantity of liquid is poured or distilled in through the other tube A. Both menisca of the liquid are gently heated with a little flame and brought to boiling, to expel all air in the tube, and, while still boiling, the neck of the tube A is sealed up.

To determine the viscosity of liquid thus filled, the viscosimeter is turned at an angle over 90 degrees, say, to the left side, so that most part of the liquid is collected in one of its limbs. Bringing it again in the vertical position, the left meniscus begins to descend, and the differences of the both menisca ($2H_1$ and $2H_2$) are determined at two different times (θ_1 and θ_2). Then the viscosity (η) of the liquid is calculated by the following formula:

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(1) Thorpe and Rodger, *Phil. Trans.*, (A) 185 (1894), 532.

(2) loc. cit.

$$\eta = k.\frac{\theta_2 - \theta_1}{\log(H_1 + \varDelta_1) - \log(H_2 + \varDelta_2)}.(D_l - D_g).(1 + \alpha t) \times 10^{-5}\ldots\ldots\ldots(1)$$

The deduction of this formula will be given later. The coefficient k is a viscosimeter-constant and independent of the temperature and the nature of the liquid employed. $\varDelta_1$ and $\varDelta_2$ are corrections due to kinetic energy, D_l and D_g are respectively the density of the liquid and vapour, α the linear expansion coefficient of glass and t the temperature of the liquid.

In order to use the same part of the viscosimeter tube in a series of observations, a pair of marks (M_1 and M_2) was etched on one of the limbs. The time of passage of the meniscus through these marks was recorded by means of a stop-watch and, at the same time, the hights of marks M_1 and M_2 and also that of the level of equilibrium were measured by a cathetometer. The values of H_1 and H_2 in the equation (1) are known from these readings.

As the apparatus is closed completely, the measurement can be done under moderately high pressure above the normal boiling point. The one and the same viscosimeter tube can repeatedly be used by opening the side tubes and filling with other substances.

With this viscosimeter several difficulties, which arise from the use of Heydweiller's, can be overcome. Above all, the viscosity of many substances such as acids and halogen or sulphur compounds, which attack mercury at all temperatures or when heated, can safely be determined by this method.

The viscosimeter was kept in a constant known temperature by heating it in a vapour-jacket, (Fig. 2). The lower end of the jacket tube G is bent and blown in a pear shaped bulb as is shown in the figure, while the upper end of which is closed by a stopper perforated with two holes. A metal rod R passes through one of the holes and is centered by two sets of small metallic pieces of the star shape. The viscosimeter V is fixed to the metal rod by a hook and a spring. Through the other hole in the stopper passes a small glass tubing T. This is connected to the pump and a big air reservoir for damping the fluctuation of pressure. Thus the liquid L in the bottom boils under reduced pressure at constant temperature. The uniformity of the temperature along the viscosimeter is secured by a wider cylindrical glass tube M placed outside the jacket tube. The temperatures are measured by a normal thermometer hanged just behind the viscosimeter.

The jacket tube is provided with a Liebig's condenser C and kept in a vertical position by the large stand P and clamps A_1 and A_2 as is shown in the figure. The stand is fixed to the table F by two steel hinges H, so that the whole apparatus may be turned about one of the edges of the stand-plate S. By this means the liquid in the viscosimeter can easily be collected in one (left one in the figure) of its limbs without allowing the liquid in the bulb to flow out nor stop boiling.

The Theory of Measurement.(1) If the difference of menisca at the time θ be $2H$ and the radius of the wider tube of the viscosimeter be R, the amount of decrease of the potential energy dE_p in the time $d\theta$ will be:

$$dE_p = -2\pi \, . \, R^2 \, . \, g \, . \, (D_l - D_g) \, . \, H \, . \, dH.$$

in which D_l and D_g are respectively the density of the liquid and vapour, g the acceleration of gravity.

The increase of kinetic energy dE_k of this system in the time $d\theta$ is mainly due to that of the liquid in both capillaries. Denoting their common radius by r, this will be:

$$dE_k = 2\pi \, . \, D_l \, . \, \frac{R^6}{r^4} \, . \left(\frac{dH}{d\theta}\right)^2 . \, dH.$$

The difference of the above two quantities will be the amount of energy dW which is converted into heat in the capillaries by internal friction. If the lengthes of the two capillaries are l_1 and l_2, this energy due to viscosity will amount to:

$$dW = -8\pi . \, (l_1 + l_2) \, . \, \eta \, . \, \frac{R^4}{r^4} \, . \, \frac{dH}{d\theta} \, . \, dH.$$

Since the algebraic sum of the above three quantities will be equal to zero, we obtain the following equation:

$$\frac{dH}{d\theta} = -\frac{g . (D_l - D_g)}{4 \, (l_1 + l_2) \, . \, \eta} \, . \, \frac{r^4}{R^2} \, . \, H \, . \times \left\{1 - \frac{1}{g . H} \, . \, \frac{D_l}{D_l - D_g} \, . \, \frac{R^4}{r^4} \, . \left(\frac{dH}{d\theta}\right)^2\right\} \ldots(2)$$

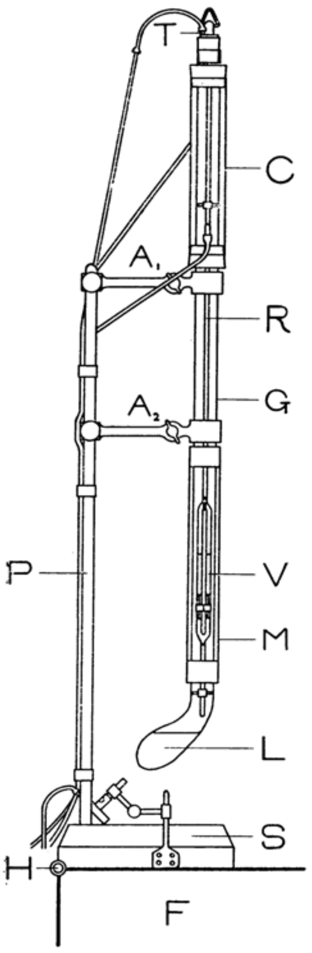

Fig. 2.

For the sake of simplicity, putting

$$\mathrm{A} = \frac{4 \, (l_1 + l_2) \, . \, \eta}{g \, . \, (D_l - D_g)} \, . \, \frac{R^2}{r^4} \, \ldots\ldots\ldots(3), \qquad \mathrm{B} = \frac{1}{g} \, . \, \frac{D_l}{(D_l - D_g)} \, . \, \frac{R^4}{r^4} \ldots\ldots\ldots(4)$$

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(1) The method of calculation used by Heydweiller was adopted. For details, see the original paper already cited.

the equation (2) becomes

$$\frac{dH}{d\theta} = -\frac{H}{A} + \frac{B}{A} \cdot \left(\frac{dH}{d\theta}\right)^2$$

As a solution of this differential equation, under suitable neglection we obtain :

$$\frac{\theta}{A} = -\ln H . \left(1 + \frac{B}{A^2} . H\right) + \text{Const.}$$

If H_1 and H_2 correspond respectively to θ_1 and θ_2, from the above we have :

$$A = \frac{\theta_2 - \theta_1}{\ln H_1' - \ln H_2'} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

In this relation

$$H' = H + \frac{B}{A^2} H^2 = H + \Delta,$$

the second term of which is evidently a correction due to the loss of the kinetic energy and can be computed by means of a successive approximation. (see equations (3) and (4)).

Let the quantities without index be refered to t° and those with index 0 to 0°, and the linear expansion coefficient of glass be a, from equations (3) and (5) we have :

$$\eta = k . \frac{\theta_2 - \theta_1}{\log H_1' - \log H_2'} . (D_l - D_g) . (1 + at) \times 10^{-5} \ldots\ldots\ldots\ldots (1)$$

in which

$$\begin{aligned} k &= 0.4343 . \frac{1}{A_0} . \frac{\eta_0}{D_{l0} - D_{g0}} \\ &= 0.4343 . \frac{g}{4\,(l_{10} + l_{20})} . \frac{r_0^4}{R_0^2}. \end{aligned}$$

This equation is identical with that which has already been given above.

Results. For the measurements of heights an accurate cathetometer made by Société Genevoise was used and times were recorded by a stop-watch provided with a stripping-index so as to eliminate errors due to inertia.

For example, the result obtained with carbon-tetrachloride will be cited below.

TABLE 1.

Carbon-tetrachloride.

t° C.	θ sec.	H_1 mm.	H_2 mm.	Δ_1 mm.	Δ_2 mm.	H_1' mm.	H_2' mm.	log η/k
20.00	52.0	36.7	22.7	0.4	0.1	37.1	22.8	$\bar{3}.5929$
30.00	46.7	36.1	22.1	0.5	0.2	36.6	22.3	$\bar{3}.5335$
30.00	47.1	36.0	22.0	0.5	0.2	36.5	22.2	$\bar{3}.5348$
40.00	42.9	35.3	21.3	0.6	0.2	35.9	21.5	$\bar{3}.4761$
40.00	43.2	35.2	21.2	0.6	0.2	35.8	21.4	$\bar{3}.4776$
50.00	40.0	34.3	20.3	0.7	0.2	35.0	20.5	$\bar{3}.4218$
50.00	40.0	34.3	20.3	0.7	0.2	35.0	20.5	$\bar{3}.4218$
60.00	37.4	33.5	19.5	0.8	0.3	34.3	19.8	$\bar{3}.3750$
60.00	37.6	33.4	19.4	0.8	0.3	34.2	19.7	$\bar{3}.3757$
70.00	35.6	32.6	18.6	0.9	0.3	33.5	18.9	$\bar{3}.3298$
76.75	34.2	32.0	18.0	1.0	0.3	33.0	18.3	$\bar{3}.2952$
80.00	33.5	31.6	17.6	1.0	0.3	32.6	17.9	$\bar{3}.2768$
90.00	32.5	30.7	16.7	1.1	0.3	31.8	17.0	$\bar{3}.2378$
100.00	31.5	29.6	15.6	1.3	0.3	30.9	15.9	$\bar{3}.1915$
110.0	30.9	28.6	14.6	1.3	0.3	29.9	14.9	$\bar{3}.1551$
120.0	30.5	27.5	13.5	1.4	0.3	28.9	13.8	$\bar{3}.1158$
130.0	30.6	26.35	12.35	1.45	0.35	27.8	12.7	$\bar{3}.0836$
140.0	31.0	25.2	11.2	1.5	0.3	26.7	11.5	$\bar{3}.0488$
150.0	31.8	23.9	9.9	1.5	0.3	25.4	10.2	$\bar{3}.0154$
160.0	33.1	22.5	8.5	1.5	0.2	24.0	8.7	$\bar{3}.9767$
170.0	35.6	21.1	7.1	1.5	0.2	22.6	7.3	$\bar{4}.9483$
180.0	39.0	19.5	5.5	1.4	0.1	20.9	5.6	$\bar{4}.9114$

The values of t and H are means of several observations. It will be seen that the time of flow decreases slowly up to 120° and then increases. Such were also seen in the other observations and will be ascribed to the combined effect of the diminution of viscosity and density of the liquid with temperature. Therefore the values of Δ_1 and Δ_2, the corrections due to the loss of kinetic energy, have maxima at high temperatures.

To calculate the absolute values of the viscosities by the equation (1), the value of the viscosimeter-constant k must be determined. For this purpose the results obtained below the boiling point (76.75°) were compared with those of Thorpe and Rodger :⁽¹⁾

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(1) T.E. Thorpe and J.W. Rodger, *Phil. Trans.*, (A), **185**, (1894), 397; ibid., **189**, (1897), 71.

TABLE 2.

Temp. t°C.	log η (Thorpe and Rodger)	log η/k (Titani)	log k (Difference)
20	$\bar{3}.9863$	$\bar{3}.5929$	0.3934
30	$\bar{3}.9251$	$\bar{3}.5335$	0.3916
30	$\bar{3}.9251$	$\bar{3}.5348$	0.3903
40	$\bar{3}.8681$	$\bar{3}.4761$	0.3920
40	$\bar{3}.8681$	$\bar{3}.4776$	0.3905
50	$\bar{3}.8152$	$\bar{3}.4218$	0.3934
50	$\bar{3}.8152$	$\bar{3}.4218$	0.3934
60	$\bar{3}.7661$	$\bar{3}.3750$	0.3911
60	$\bar{3}.7661$	$\bar{3}.3757$	0.3904
70	$\bar{3}.7193$	$\bar{3}.3298$	0.3895
			Mean 0.3916

In the case of ethyl alcohol, a similar comparison with the same authors' values gave log $k = 0.3936$, the average of the two being log $k = 0.3926$, which value was used in the case of chlorobenzene, where no reliable standard data below the boiling point were found. The values of viscosity of the above three substances expressed in dyne per square centimeter are summarised below, together with those of methyl-acetate and fluorobenzene which were formerly determined by Heydweiller's method. The values of density necessary for the determination of viscosity were all obtained from the data of S. Young.(1) The viscosities in the second column are the values directly observed and those in the third (or fourth) are the values interpolated (or slightly extrapolated) from curves. In the fourth (or fifth) column are given the results obtained by other observers for the purpose of comparison.

TABLE 3.

Methyl-acetate. B.P. = 57°.0.

Temp. t°C.	η Observed value	Temp.	η From curves	η Thorpe and Rodger(2)
		0	—	0.00478
19.5	0.00386	10	—	0.00425
20.3	0.00382	20	0.00381	0.00381
34.5	0.00328	30	0.00344	0.00344
		40	0.00312	0.00312

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(1) S. Young, *Sci. Proc. Roy. Dublin Soc.*, [New Series] 12 (1909—1910), 374.

(2) loc. cit. These values were used to compute the viscosimeter-constant.

TABLE 3. *Continued.*

Methyl-acetate.

Temp. t°C.	η Observed value	Temp.	η From curves	η Thorpe and Rodger
46.1	0.00294			
		50	0.00284	0.00284
56.7	0.00267			
60.3	0.00258	60	0.00258	—
65.0	0.00249			
		70	0.00237	—
80.4	0.00217	80	0.00217	—
		90	0.00198	—
		100	0.00182	—
110.2	0.00167	110	0.00166	—
		120	0.00154	—
		130	0.00142	—
139.0	0.00132	140	0.00130	—

TABLE 4.

Carbon-tetrachloride. B.P. = 76°.75.

Temp. t° C.	η Observed value	η From curves	η Thorpe and Rodger
0.00	—	—	0.01347
10.00	—	—	0.01133
20.00	0.00965	0.00969	0.00969
30.00	0.00843	0.00843	0.008415
40.00	0.00739	0.00739	0.00738
50.00	0.00651	0.00651	0.006535
60.00	0.00585	0.00585	0.005835
70.00	0.00527	0.00524	0.00524
76.75	0.00486	0.00486	0.00488*
80.00	0.00466	0.00468	—
90.00	0.00426	0.00426	—
100.00	0.00383	0.00384	—
110.0	0.00352	0.00352	—
120.0	0.00322	0.00323	—
130.0	0.00299	0.00299	—
140.0	0.00276	0.00276	—
150.0	0.00255	0.00255	—
160.0	0.00234	0.00234	—
170.0	0.00219	0.00217	—
180.0	0.00201	0.00201	—

* Extrapolated value.

Table 5.

Fluorobenzene. B.P. = 84.°8.

Temp. t° C.	η Observed values	Temp. t° C.	η From curves	η Meyer and Mylius(1)
		0	—	0.00755*
		10	—	0.00647
		20	0.00598	0.00584
25.7	0.00561			
		30	0.00532	0.00519
		40	0.00478	0.00471
46.8	0.00443			
		50	0.00428	0.00427
60.5	0.00388			
		60	0.00389	0.00388
64.7	0.00371			
		70	0.00357	0.00355
80.4	0.00330	80	0.00329	0.00327
		90	0.00300	—
100.2	0.00275	100	0.00275	—
110.0	0.00249	110	0.00250	—
		120	0.00231	—
130.8	0.00213	130	0.00214	—
136.1	0.00203			
		140	0.00198	—
136.3	0.00202			
		150	0.00182	—
155.2	0.00176			
		160	0.00168	—
		170	0.00156	—
182.0	0.00141	180	0.00144	—

* Recalculated from the values $1/\eta$ given by Meyer and Mylius.

Table 6.

Chlorobenzene. B.P. = 131.°74.

Temp. t° C.	η Observed values	η From curves	η Meyer and Mylius
10.0	—	0.00907	0.00912*
12.5	0.00876	—	—
20.0	0.00799	0.00799	0.00805
30.0	0.00715	0.00705	0.00710
40.0	0.00631	0.00631	0.00638
50.00	0.00571	0.00567	0.00580
60.00	0.00512	0.00515	0.00526
70.00	0.00472	0.00471	0.00481
80.00	0.00431	0.00431	0.00441
90.00	0.00397	0.00397	0.00405
100.00	0.00367	0.00367	0.00376
110.0	0.00339	0.00339	0.00351
120.0	0.00313	0.00313	0.00327
130.0	0.00292	0.00293	0.00306
131.7	0.00287	0.00288	—

* Interpolated from the curve drawn with the data given by Meyer and Mylius (loc. cit.).

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(1) J. Meyer and B. Mylius, *Z. physik. Chem.*, 95 (1920), 349. These values were used to compute the viscosimeter-constant.

TABLE 6. *Continued.*

Chlorobenzene. B.P. = 131°.74.

Temp. $t°$ C.	η Observed values	η From curves	η Meyer and Mylius
140.0	0.00273	0.00274	—
150.0	0.00257	0.00256	—
160.0	0.00239	0.00239	—
170.0	0.00222	0.00223	—
180.0	0.00209	0.00209	—
190.0	0.00196	0.00196	—
200.0	0.00186	0.00185	—
210.0	0.00173	0.00173	—
220.0	0.00162	0.00163	—
230.0	0.00155	0.00153	—
240.0	0.00144	0.00144	—

TABLE 7.

Ethyl alcohol. B.P. = 78°.27.

Temp. $t°$ C.	η Observed values	η From curves	η Thorpe and Rodger
0.00	—	—	0.01770
10.00	—	—	0.01449
20.00	—	—	0.01192
30.00	0.00991	0.00991	0.009895
40.00	0.00823	0.00825	0.008275
50.00	0.00701	0.00701	0.006975
60.00	0.00591	0.00591	0.005915
70.00	0.00503	0.00503	0.005045
78.27	0.00442	0.00446	0.00441*
80.00	0.00435	0.00435	—
90.00	0.00376	0.00376	—
100.00	0.00325	0.00325	—
110.0	0.00285	0.00283	—
120.0	0.00247	0.00248	—
130.0	0.00217	0.00217	—
140.0	0.00193	0.00191	—
150.0	0.00166	0.00166	—

* Extrapolated value.

Summary.

1. The viscosities of methyl-acetate and fluorobenzene were determined above their boiling points after the method described by A. Heydweiller.

2. To overcome several difficulties which arise from the use of his apparatus, a new viscosimeter was devised.

3. By means of this apparatus, the viscosities of carbon-tetrachloride, chlorobenzene and ethyl alcohol were determined above their boiling points.

In conclusion, the author wishes to express his cordial thanks to Prof. M. Katayama for his kind guidance.

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January, 1927. Hongo, Tokyo.