THE VISCOSITY OF VAPOURS OF ORGANIC COMPOUNDS. PART I.

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The viscosity of several organic liquids were already measured by the writer at temperatures extending over their boiling points.[1] The present work concerns with the viscosity of organic compounds in gaseous state. The object is not only to supply reliable data in respective states of aggregation, but also to compute the diameters of molecules from these observations. The temperature coefficient of viscosity which is specially important in this case has been determined with great care.

Theory of the Method. One of the most prevalent principle to determine the viscosity of gases and vapours is that of transpiration. This principle was used by Pedersen,[2] Rappenecker[3] and Rankine[4] in their well-known works. On the same principle is based also the viscosimeter devised by the writer, the principal part of which is diagramatically illustrated in Fig. 1. The fine glass capillary tubes, each having internal diameter of about 0.194 mm. and length of 39.5 cm. respectively, are connected below by a wider U-tube. The upper end of each capillary tube is fused on to a wider uniform glass tube bent to the vertical position parallel to the capillaries. The inner diameters of both wider limbs are almost equal with each other, being about 1.86 mm. Two marks, M_1 and M_2,

Fig. 1.

(1) This Bulletin, **2** (1927), 95; ibid., 161; ibid., 196; ibid., 225; **4** (1929), 68.
(2) Pedersen, *Phys. Rev.*, **25** (1907), 225.
(3) Rappenecker, *Z. physik. Chem.*, **72** (1910), 695.
(4) Rankine, *Proc. Roy. Soc. London*, [A], **83** (1910), 265.

are etched on the right limb a distance of about 27 cm. apart, containing about 0.73 c.c. between them.

A short mercury-column is placed in each wider limb respectively, its length being chosen as equal as possible. The space between these two columns is filled with the gas to be examined. If we connect the right limb of the viscosimeter to a constant pressure source slightly higher than one atmosphere and let the left one open to air, the equilibrium is broken, the right mercury-column H_1 being pushed up driving the gas above it through the capillaries, so that the left column H_2 is pushed down; and vice versa. The times required by the right column to pass through the two marks are successively recorded, t_1 denoting the upward and t_2 the downward. From each of these two recorded times, the viscosity η of the gas may be calculated by the following formulae.

$$\frac{\eta}{k}=\frac{P^2-p^2}{P}\cdot t_1 \quad \text{up} \quad (1)$$

$$\frac{\eta}{k}=\frac{P^2-p^2}{p}\cdot t_2 \quad \text{down} \quad (2)$$

$$k=\frac{\pi g r^4}{16\, lv} \quad (3)$$

Corrections for slipping and kinetic energy were found to be within the limit of the experimental error. The apparatus constant k expressed by equation (3) contains the radius r and length l of the capillaries and the volume v between the two marks. By P and p are expressed respectively the effective driving pressures at the inlet and the outlet of the capillary U-tube. These effective pressures P and p may differ from the pressure outside of the mercury-columns minus their lengths, because the moving mercury-columns have some resistance, mainly due to capillarity at their end-surfaces and also probably due to their friction against the walls of the tubes. Elimination of this complicated resistance is one of the most difficult but important matters in this type of viscosimeter. Though an allowance was made by Pedersen only for the friction of the mercury-column against the wall, this was neglected by Rankine who took only an account for the resistance due to capillarity. On the other hand both sorts of resistances were completely neglected by Rappenecker in his works with Pedersen's viscosimeter. This unknown resistance of mercury-columns has been eliminated by the writer in the following way.

Substituting for the true effective pressures P and p in equations (1) and (2) the apparent pressures P' and p' which are equal to the outer pressure minus the lengths of the mercury-columns but not their resistance, we obtain apparent viscosities η' instead of the true one η by equations (4) and (5).

$$\left(\frac{\eta'}{k}\right)_1=\frac{P'^2-p'^2}{P'}t_1 \text{ .... up .... } (4)$$

$$\left(\frac{\eta'}{k}\right)_2=\frac{P'^2-p'^2}{p'}t_2 \text{ ....down .... } (5)$$

The apparent viscosities so calculated are no more independent of the driving pressure but decrease as the latter increases. It was found by the writer experimentally that the reciprocal of the apparent viscosity $\frac{k}{\eta'}$ is a linear function of the reciprocal of the apparent driving pressure $\left(\frac{1}{P'-p'}\right)$.

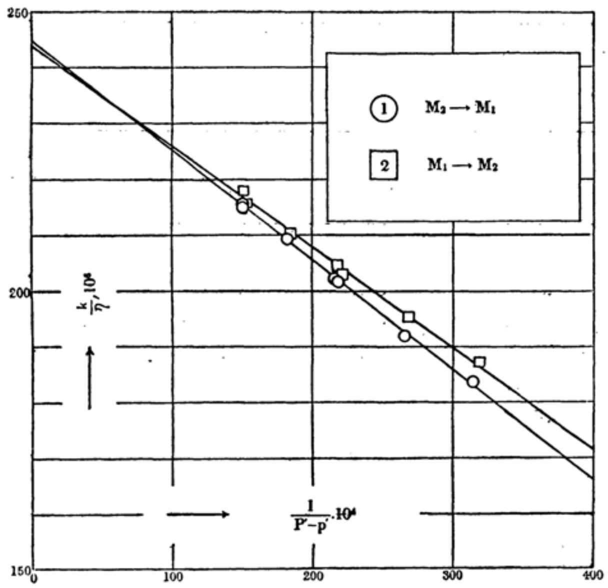

Fig. 2.

This is illustrated in Fig. 2, in which the former is plotted as ordinate and the latter as abscissa, each straight line corresponding to the case of pushing up or down. This relation may be seen more clearly in the following example.

Table 1. Air at 20°C.

Length of the mercury-columns: right=26.5 mm., left=26.7 mm.

(1) The case of pushing up.

P'	p'	t_1 sec.	$\frac{1}{P'-p'}$	$(k/\eta')_1\cdot10^6$	
				Obs.	Calc.
—	—	0	0	—	244.8
803.2	736.3	36.2	0.01495	215.4	215.3
803.7	736.9	36.3	1497	215.1	215.2
791.6	736.6	45.0	1818	209.3	208.9
783.1	736.5	54.7	2146	202.1	202.4
782.9	737.1	55.8	2183	201.6	201.7
774.4	736.7	70.9	2653	191.7	192.4
768.5	736.6	87.2	3135	183.6	182.9

(2) The case of pushing down.

P'	p'	t_2 sec.	$\frac{1}{P'-p'}$	$(k/\eta')_2\cdot10^6$	
				Obs.	Calc.
—	—	0	0	—	243.8
803.0	736.5	33.0	0.01504	218.0	216.5
803.5	737.1	33.4	1506	215.6	216.5
791.4	736.8	42.0	1832	210.2	210.6
782.9	736.7	51.3	2165	204.6	204.6
782.7	737.3	52.6	2203	203.1	203.9
774.2	736.9	67.0	2681	195.1	195.2
768.3	736.8	83.1	3175	187.1	186.3

The values in the last columns were calculated by the following equations,

$$(1)\quad (k/\eta')_1\cdot10^6=244.8-1975\frac{1}{P'-p'}\ \cdots\cdots\cdots\ \text{up.}$$

$$(2)\quad (k/\eta')_2\cdot10^6=243.8-1812\frac{1}{P'-p'}\ \cdots\cdots\cdots\ \text{down.}$$

or expressed in general form:

$$(k/\eta')_1 \cdot 10^6 = \frac{1}{a_1} - \frac{b_1}{P'-p'} \quad \text{........... up ....} \quad (6)$$

$$(k/\eta')_2 \cdot 10^6 = \frac{1}{a_2} - \frac{b_2}{P'-p'} \quad \text{...........down ....} \quad (7)$$

The first terms in the right hand side express the limiting values of apparent fluidity k/η' when the driving pressure becomes infinite, where all sorts of resistances of mercury-columns can safely be neglected, so that these limiting values give the true relative fluidity k/η. As exactly equal values for $\frac{1}{a_1}$ and $\frac{1}{a_2}$ could not be obtained practically, the mean of the two graphically extrapolated values from the observations under various driving pressures was taken as the final result.

$$k/\eta \cdot 10^6 = \frac{\frac{1}{a_1} + \frac{1}{a_2}}{2} \quad \text{..........................} \quad (8)$$

For example in the above case of air we have:

$$k/\eta \cdot 10^6 = \frac{244{\cdot}8 + 243{\cdot}8}{2} = 244.3\,.$$

Although this way of computation was first obtained solely experimentally, it can be shown that exactly the same result is deduced theoretically under some plausible assumptions.

If we assume the resistances of the right and left mercury-columns being expressed by Δ and $\Delta+\delta$ respectively, it will easily be seen from Fig. 1 that, in the case of pushing up, the true effective pressures P and p are related with apparent pressures P' and p' by the following equations.

$$P = P' - \Delta\,, \qquad p = p' + \Delta + \delta\,. \quad \text{.................} \quad (9)$$

Substituting these relations for P' and p' in eq. (4), we have

$$(\eta'/k)_1 = t_1 \frac{P'^2 - p'^2}{P'} = t_1 \frac{(P+\Delta)^2 - (p-\Delta-\delta)^2}{P+\Delta}$$

$$= t_1 \frac{P^2 - p^2}{P} \cdot \frac{\left(1 + \frac{2P\Delta + 2p\Delta + 2p\,\delta}{P^2 - p^2}\right)}{1 + \frac{\Delta}{P}} \quad \text{.............} \quad (10)$$

This is the exact solution, but it contains not only the unknown value Δ but also that of δ. Now we assume that the resistances of both columns are equal, i.e. δ is zero. This assumption seems very plausible if we take the following facts into consideration. First of all, the capillarity of both columns may be acknowledged to be equal with each other. Because the diameters of both mercury limbs are practically the same, as they are made of one long uniform tube by cutting it in the middle; and also a little difference in the section may have little influence, since the curvature of the meniscus of a moving mercury becomes larger in the smaller diameter and vice versa. In the second place it was found by the preliminary research that a fairly large difference in lengths of columns has no effect on the resultant resistance, so that the resistance due to friction is considered to be of second order compared with that due to capillarity. Thus, putting $\delta=0$ in eq. (10) and considering that the first factor in the right hand side is equal to η/k, it becomes

$$(\eta'/k)_1=(\eta/k)\frac{1}{1+\dfrac{\Delta}{P}}\left(1+\frac{2\Delta}{P-p}\right). \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (11)$$

Substituting for P and p in this equation the relations (9) and reverting both sides of the equation thus obtained, we have

$$(k/\eta')_1=\frac{k}{\eta}\cdot\left(1+\frac{\Delta}{P}\right)\cdot\left(1-\frac{2\Delta}{P'-p'}\right). \quad \ldots\ldots \text{ up } \ldots\ldots \quad (12)$$

In exactly the same way, in the case of pushing down we have

$$(k/\eta')_2=\frac{k}{\eta}\cdot\left(1-\frac{\Delta}{p}\right)\cdot\left(1-\frac{2\Delta}{P'-p'}\right). \quad \ldots\ldots \text{ down } \ldots\ldots \quad (13)$$

These two equations are nothing but eqs. (6) and (7), if we assume the second factors $\left(1+\dfrac{\Delta}{P}\right)$ and $\left(1-\dfrac{\Delta}{p}\right)$ are constant within the range of pressures applied. Comparing above eqs. (12) and (13) with (6) and (7) respectively, it follows:

$$\frac{\dfrac{1}{a_1}+\dfrac{1}{a_2}}{2}\cdot 10^{-6}=\frac{\dfrac{k}{\eta}\left(1+\dfrac{\Delta}{P}\right)+\dfrac{k}{\eta}\left(1-\dfrac{\Delta}{p}\right)}{2}\doteqdot k/\eta\,, \quad \ldots\ldots \quad (14)$$

and $$b_1=\frac{2\Delta}{a_1}\,, \qquad b_2=\frac{2\Delta}{a_2}\,. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (15)$$

Eq. (14) corresponds to formula (8) and the column-resistance Δ can be computed by eq. (15). This value was found to be about 4 mm. Hg, this being of quite reasonable order as compared with ordinary capillary depression.

Description of the Apparatus. The general view of the apparatus used is shown in Fig. 3. The viscosimeter V is supported by a rubber stopper S in a vapour jacket F and heated to a constant temperature by the vapour of the boiling liquid L. The vapour jacket is surrounded by a wider glass cylinder not shown in the figure, the cylinder being partially covered by cotton wool and asbestos paper. The heating liquid is introduced through a bent tube I and heated by a spiral of nichrom wire E. Some

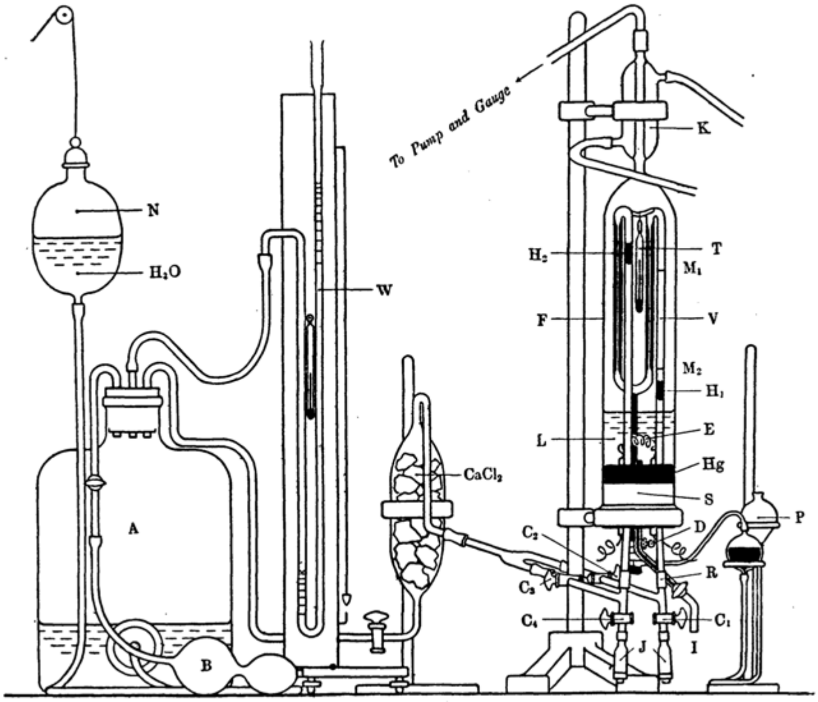

Fig. 3.

mercury is placed on the rubber stopper to prevent the liquid touching it. The upper end of the jacket is fused on to a Liebig's condenser K, the upper end of which being connected to a big air reservoir, a pump and a manometer. By means of them the pressure in the jacket can be regulated to keep the vapour at desired temperature. A thermometer T is hanged from the top of the viscosimeter and serves also as a plumb line.

The capillaries of the viscosimeter are bent behind so as to spare the space as possible. A vertical central limb shown black in the figure passes through the stopper and is connected through a two way tap D to a small mercury pot. This tube was introduced for the purpose of cleaning and filling of the viscosimeter by means of a mercury reservoir P. Both limbs containing the indicating mercury-columns also pass through the stopper and their lower end are connected by means of rubber stoppers R to a commutating devise. It consists of a pair of T-shaped tubes, each of which being provided with two stop-cocks C_1, C_2 or C_3, C_4. By means of this devise either limb can be turned to the driving pressure at C_2 or C_3, or to air at C_1 or C_4. Two $CaCl_2$-tubes J are placed at the openings to air. A compressed air from the reservoir A is dried by passing it through a $CaCl_2$-tower, whence being lead through a wide Y-shaped tube to the commutating taps C_2 and C_3. The pressure in the reservoir A is controlled by means of a water vessel N and a hand-bellows B and is measured on the water manometer W. The reservoir is packed round with cotton wool and put in a wooden box.

In this type of viscosimeter it is specially important that the mercury limbs should be quite clean, or the mercury-columns will stick and move with jerks. Standing over a night or more with freshly prepared concentrated chromic mixture was found very effective for this purpose. Great care was taken to prevent some dust particles or greasy matter entering into the viscosimeter during washing and drying.

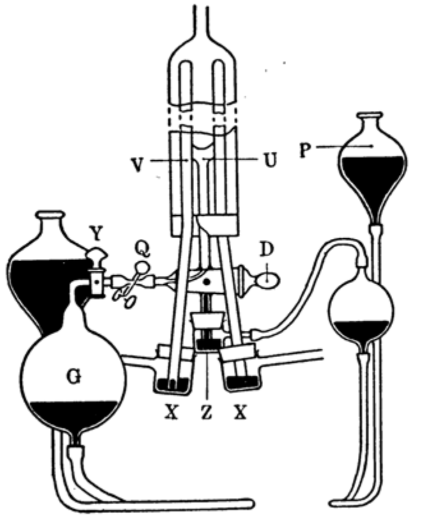

Fig. 4.

In order to fill the viscosimeter with the gas to be examined, the commutating devise is removed and the lower end of each mercury limb is dipped respectively in a pot (X in Fig. 4) containing some clean mercury. To the end of the central limb is also fixed a small mercury pot Z, to which a pressure is applied by means of a mercury reservoir P. The two way tap D is at first turned to its side tube, which is connected to the gas reservoir G of about 150 c.c. capacity. Keeping proper pressure in the reservoir and opening taps Q and Y, the gas is forced into the viscosimeter, the excess bubbling out through the mercury in the pots X, until all the air in the viscosimeter is completely expelled. Then the pinch-cock Q is closed and the pressure in the reservoir is somewhat lowered, after which Q is opened for a moment to suck up a small quantity of mercury from pots X. As soon as desired amounts are taken, the mercury pots are quickly removed, and the pinch-cock Q is sufficiently opened to suck up the mercury columns at a suitable height. The two way tap D is then turned, so that the mercury in the pot Z is allowed to run up into the central limb just to the blanching point U. The viscosimeter is now ready for measurement. The length of mercury column can be calculated from the loss of the weight of the pot X by multiplying it with suitable coefficient obtained by the preliminary determination.

After each filling, the movability of mercury columns has been tested repeatedly during one hour, before the actual measurement begins. This preliminary tests are necessary to secure the steady state.

Experiment with Air. At first an experiment was done with dry air free from carbon dioxide, in order to test the method and to find the viscosimeter-constant. The results are shown in the following table.

Table 2.

t°C	$\frac{1}{a_1}$	b_1	$\frac{1}{a_2}$	b_2	$\frac{1}{a}$	(η/k)
20°	244.8	1975	243.8	1812	244.3	4093
40	234.5	1999	231.6	1830	233.0	4292
60	220.7	1806	219.8	1788	220.2	4541
80	211.0	1734	214.3	1902	212.6	4704
100	204.6	1719	202.9	1639	203.8	4907

The values $\frac{1}{a}$ in the sixth column are the means of the two limiting values $\frac{1}{a_1}$ and $\frac{1}{a_2}$, and those in the next column are the reciprocal of $\frac{1}{a}$ multiplied by 10^6. This is the true relative viscosity η/k, and can be expressed by the following Sutherland's formula:

$$\eta/k = 330.9\frac{T^{3/2}}{T+112.6}\ .$$

The viscosimeter-constant k is known from the calculated value of η/k at 23°C. and the known absolute value at the same temperature given by Millikan.

$$(\eta/k)_{23} = 330.9 \frac{(296.1)^{3/2}}{296.1 + 112.6} = 4125\ ,$$

$$\eta_{23} = 1823 \times 10^{-7}\ \text{(Millikan)}\ ,$$

$$\therefore\ \ k = 0.4419 \times 10^{-7}.$$

The relative values of viscosity η/k in Table 2 can now be expressed in absolute unit, which is shown in the following table.

Table 3.

Air $\quad \eta = 146.3 \frac{T^{3/2}}{T + 112.6} \cdot 10^{-7}$

t°C	$\eta \cdot 10^7$	
	Obs.	Calc.
0	—	1711
20	1809	1809
40	1897	1903
60	2007	1995
80	2079	2084
100	2169	2170

It will be seen that the above values agree well with values given by other observers.

Table 4.

Sutherland's Constant C of Air.

113 (Sutherland)	107 (Pedersen)
111 (Rayleigh)	119 (Rappenecker)
119 (Breitenbach)	113 (K. Schmitt)
116 (Rankine)	117 (Rankine & Smith)
124 (Fisher)	113 (Titani)

Table 5.

The Viscosity of Air at 0°C.

$\eta_0 \cdot 10^7$	Observers
1683	Graham (1846)
1678	v. Obermayer (1875)
1733	Breitenbach (1901)
1802*	Pedersen (1907)
1736	Zimmer (1912)
1726*	Kuenen and Visser (1913)
1724	Vogel (1914)
1724	Smith (1922)
1725	Klemenc and Remi (1923)
1711*	Ishida (1923)
1735*	Trautz and Weizel (1925)
1711	Titani (1929)

An advantage of the writer's method is that the viscosity of a gas available only in a small quantity can be measured at various temperatures with single filling. The viscosities of the following seventeen gases have been determined with this apparatus at several temperatures between 20° and 120°C:

Ethane, propane, *n*-butane, isobutane, ethylene, propylene, α-butylene, β-butylene, γ-butylene, isoamylene, acetylene, allylene, trimethylene, methyl-ether, methyl-chloride, methyl-bromide and sulphur-dioxide.

The results of the measurements will be reported in the second part of this paper.

In conclusion, the writer wishes to express his cordial thanks to Prof. M. Katayama for his kind guidance and encouragement throughout this experiment.

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