[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Drainage Error in Viscometry of Aqueous Solutions

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The determination of the viscosity of aqueous solutions relative to that of pure water by means of the Ostwald viscometer is based on the assumption that identical volumes of solution and of pure water are delivered by the measuring bulb in the comparative measurements. This assumption is not rigorously exact since, as long has been recognized,[1] a drainage error may occur whose magnitude will depend in each case upon a variety of factors, such as shape and volume of the bulb, the temperature, the time of outflow, the viscosity, the density and perhaps the surface tension of the liquid. The data in the literature on this subject are mostly concerned with heavy oils many times more viscous than water. Furthermore, the conclusions reached by various investigators are somewhat contradictory. Drainage errors of course also occur and are of great importance in volumetric analysis. Certain of their aspects in this connection have been studied repeatedly.[2]

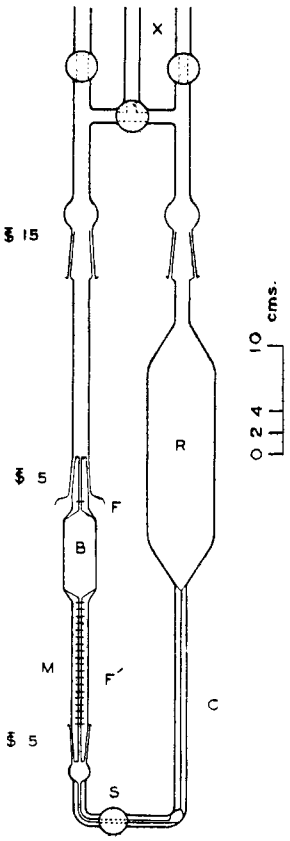

Fig. 1.

A number of improvements in the technique of viscometry have recently been made in this Laboratory[3] in connection with a series of measurements upon aqueous solutions. These improvements have resulted in a considerable increase in the precision attainable by means of the Ostwald viscometer, and have made it desirable to ascertain more accurately the magnitude of the drainage error. We report herewith on a series of measurements carried out for this purpose.

The *absolute* drainage error is the volume between the upper and lower timing marks on the measuring bulb of the viscometer minus the volume of liquid actually delivered under the conditions of the experiment, divided by the total volume. The *relative* drainage error is, of course, the difference between the absolute drainage error of the liquid under investigation and that of the standard liquid, water. The drainage error can most conveniently be determined experimentally in two parts: (a) the "after-drainage" which will drain out of the measuring bulb during a protracted period following the passage of the meniscus; and (b) the "wetting film" which remains on the inner surface even after this protracted drainage.

Experimental

In this series of measurements of the influence of the time of outflow and the composition and properties of the liquid upon the rate and total volume of after-drainage and the residual film remaining after protracted drainage, we have used a special viscometer (Fig. 1) of Pyrex glass with a bulb, B, of approximately 16-ml. capacity and of a shape similar to that of the vitreous silica viscometers used in our previous measurements above referred to. There is no reason to suppose that the drainage from a glass surface will differ from the drainage from a similar vitreous silica surface. The bulb drained into a tube, M, of 2.1-mm. bore with graduations in hundredths of milliliters spaced about 2.8 mm. apart. The pipet (*i. e.*, the measuring bulb and attached graduated tube) was connected through ground joints as shown to a stopcock, S; to a capillary tube, C, about 0.05 cm. in diameter and 19 cm. long; to a reservoir, R; and to a cross head, X; provided with stopcocks which made it possible to connect either the bulb, B, or the reservoir, R, to the outside atmosphere, or to a large tank of air, compressed to any desired pressure up to 10 cm. of mercury and maintained at constant pressure by a regulator of the type described by Bingham.[4] The viscometer is mounted inside a thermo-

(1) E. C. Bingham and H. L. Young, *J. Ind. Eng. Chem.*, **14**, 1130 (1922); W. H. Herschel, *J. Opt. Soc. Am.*, **6**, 875 (1922); M. R. Cannon and M. R. Fenske, *Oil and Gas Journal*, April 11, 52 (1935); see also W. B. McCluer and M. R. Fenske, *Ind. Eng. Chem.*, **27**, 83 (1935); W. E. J. Broom, *J. Inst. Petr. Techn.*, **22**, 23 (1936); L. Ubbelohde, *ibid.*, **19**, 413 (1933); see also L. Ubbelohde, *Ind. Eng. Chem., Anal. Ed.*, **9**, 88 (1936).

(2) W. Schloesser, *Z. anal. Chem.*, **46**, 392–414 (1907); *Z. angew. Chem.*, **21**, 833 (1908); *Chem. Z.*, **30**, 1071–1073 (1906); V. Stott, *J. Soc. Glass Techn.*, **5**, 307 (1921); **7**, 169 (1923); N. S. Osborne and B. H. Veazey, *Bull. Bur. Standards*, **4**, 553 (1908).

(3) Grinnell Jones and collaborators, THIS JOURNAL, **51**, 2950 (1929); **55**, 624, 4124 (1933); **57**, 2041 (1935); **58**, 619 (1936); **58**, 2558 (1936); **59**, 484 (1937); see also *Physics*, **4**, 215 (1933).

(4) E. C. Bingham, "Fluidity and Plasticity," McGraw-Hill Book Co., New York, 1922, p. 304.

stat having plate glass walls in front and rear and maintained at 25°.

The stopcock, S, can be opened or closed rapidly at any instant by a coiled spring mechanism having an electromagnetic release, which is controlled by touching an electric contact key. This same contact key makes a record of the time on the moving tape of a chronograph. A good pendulum clock records seconds on the same tape by another pen.

The viscometer was first cleaned and dried, about 25 cc. of the liquid to be studied added, the instrument mounted in the thermostat and connected to the pressure tank. The measuring bulb was then filled and the upper meniscus brought to the mark, F. The cocks in the cross head were adjusted so that the pressure desired was applied to the liquid in the bulb, and the reservoir, R, was opened to the outside air. Then the flow was started by touching the contact key which opened the stopcock, S, and recorded the time. When the meniscus reached some predetermined graduation mark on the pipet below the bulb, the contact key was again touched which closed the cock, S, and thus stopped the outflow and recorded the time. The lowest position of the meniscus was observed and read on the graduated scale, and the rise of the meniscus due to drainage of the liquid from the walls of the bulb was observed as a function of the time. A Gaertner M930 cathetometer with a M508 telescope was used to observe the meniscus. When the meniscus became tangential to the cross hair in the telescope eyepiece, the time was recorded on the chronograph tape. The micrometer eyepiece of the cathetometer was then turned through a definite interval, thus raising the cross hair by an amount which corresponded to a known volume in the pipet, and the time again recorded when the meniscus reached this new position. This process was repeated until drainage ceased, which often required about one-half hour. Then the pipet was drained completely, the viscometer removed from the thermostat and taken apart at the ground joints, and after removing the drop of liquid in the tip, if present, the pipet was quickly capped, dried externally and weighed. The difference between this weight and the dry weight gave the weight of liquid which wetted the inside of the pipet after prolonged drainage. The entire experiment could then be repeated either with the same pressure as a check or with a different pressure and therefore a different time of outflow. After the behavior of water had been measured with the time of outflow varied over the range from 27.2 seconds up to 411 seconds, the water was replaced by 20 and 40% sucrose solutions, and 1.43 molar calcium ferrocyanide solution.

Curves showing the rate of drainage for water are shown in Fig. 2; the numbers above the separate curves are the times of outflow. Although the printed graph only shows the after-drainage during the first eight hundred seconds, the observations were continued until drainage ceased. Curves for the other liquids studied are omitted to save space in printing since they are similar to those for water. They resemble curves found by Stott, and by Osborne and Veazey in experiments on the drainage of water from pipets and burets.

In Fig. 3 the data for the total after-drainage, ΔV, are plotted against the reciprocal of the

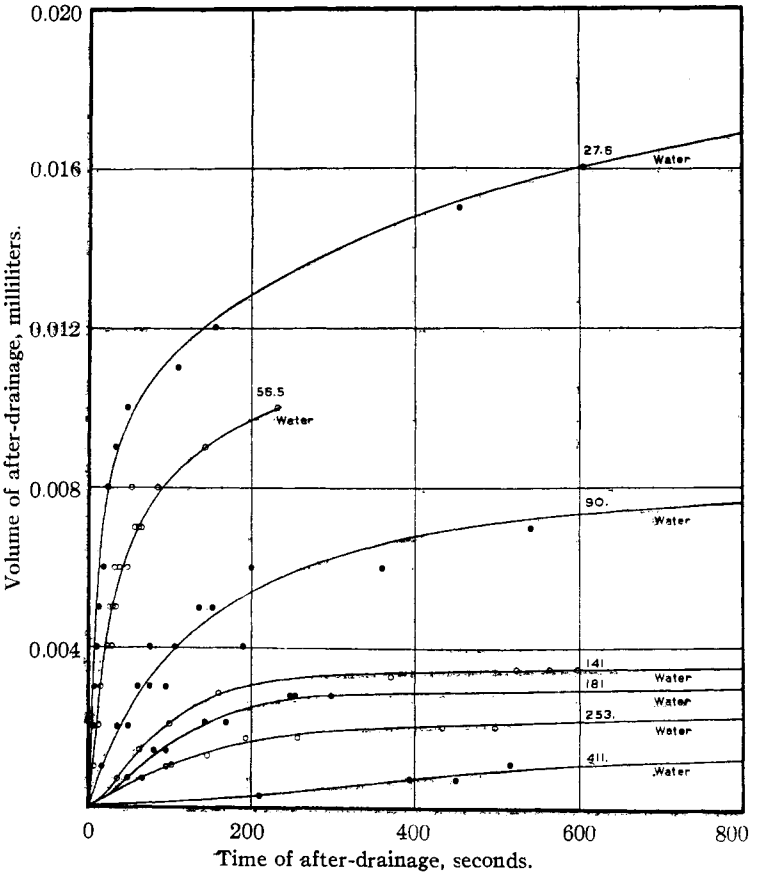

Fig. 2.—Rate of after-drainage for water with various periods of outflow.

time of outflow, giving a straight line which passes through the origin for water and for each of the solutions studied. This shows that in the region experimentally studied we may write $\Delta Vt = K$. The values of K are shown in Table I. As will be seen these values show no systematic trend and agree within the limit of experimental error, which may amount to 10 or 15% on account of the small volumes being measured.

The values of K are, however, different for water and for each of the solutions, but the value

of K turns out to be proportional (at least to an approximation of 10% which is perhaps no greater than the experimental error) to the viscosity divided by the density, η/d, or the so-called kinematic viscosity. Using a subscript c to designate a solution of concentration c, and a subscript 0 to designate water, we may write

$$\Delta V_0 t_0 = K_0 = a_0\eta_0/d_0$$

and

$$\Delta V_c t_c = K_c = a_c\eta_c/d_c$$

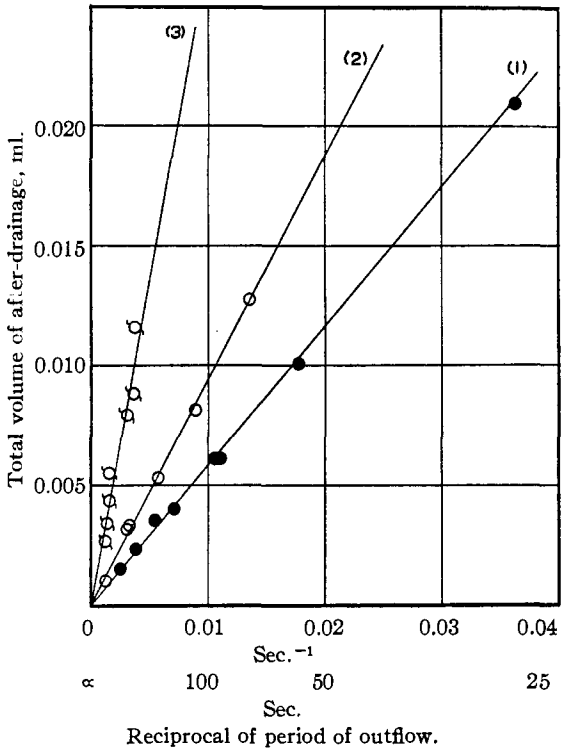

Fig. 3.—Influence of period of outflow on the total volume of after-drainage.

Now if $a_c = a_0$, as the data seem to show is true, it is easy to derive the conclusion that after-drainage can cause no error in viscosity measurements of the relative viscosity of solutions if carried out in a viscometer which depends on the hydrostatic head for the driving pressure. Omitting the small kinetic energy correction which is negligible for the present purpose, we have for such an instrument $\eta_c/\eta_0 = d_c t_c/d_0 t_0$, which combined with the equations above gives $\Delta V_c = a_c \Delta V_0/a_0$. Then if $a_c = a_0$, it follows that $\Delta V_c = \Delta V_0$, which means that the volume of the after-drainage is the same for the solution as for the water, and, therefore, there is no error in viscosity measurements due to after-drainage. This fortunate result is of course due to an automatic compensation. The more viscous solution which drains more slowly is automatically given a suitably longer time for its drainage. For viscometers which are actuated by an outside gas pressure instead of their own hydrostatic pressure, this automatic compensation is not quite so good, but does occur to a considerable extent.

TABLE I

TOTAL AFTER-DRAINAGE AT VARIOUS OUTFLOW TIMES FOR SEVERAL LIQUIDS

Outflow time in seconds, t	Volume of after-drainage in ml., ΔV	$\Delta Vt = K$	$a = \frac{\Delta V t d}{\eta}$
	Water		
27.6	0.0219	0.60	
56.5	.010	.57	
90.0	.006	.54	
94.0	.0061	.57	
141.0	.0040	.56	
181.0	.0035	.63	
253.0	.0023	.58	
411.0	.0015	.62	
		.58	0.58
20% Sucrose, η_c/η_0 = 1.9106; d_c/d_0 = 1.0876; σ_c/σ_0 = 1.014			
74	0.0127	0.94	
112	.0081	.91	
177	.0053	.94	
313	.0033	1.03	
322	.0032	1.03	
810	.0010	0.81	
		0.94	0.58
40% Sucrose, η_c/η_0 = 5.8168; d_c/d_0 = 1.1779; σ_c/σ_0 = 1.029			
261	0.0116	3.0	
270	.0088	2.4	
320	.0079	2.5	
640	.0055	3.5	
665	.0043	2.9	
736	.0034	2.5	
815	.0027	2.2	
		2.7	0.55
1.43 Molar $Ca_2Fe(CN)_6$, η_c/η_0 = 15.1; d_c/d_0 = 1.2916			
244	0.0245	6.0	0.52

On the other hand, if we assume that the difference between the value for water and 40% sucrose solution shown in Table I is real rather than due to experimental error it is easy to show that the effect on the viscosity measurements is negligible. If we use the values for a shown in the table we have $\Delta V_c = 0.55\ \Delta V_0/0.58 = 0.95\Delta V_0$. But with the instrument which we have used for viscosity measurements the volume of the measuring bulb is 10.0 ml. and the

time of outflow for water is four hundred and twenty-eight seconds and since $\Delta V_0 t = 0.58$ for water (see Table I), $\Delta V_0 = 0.00136$ and hence $\Delta V_c = 0.00129$. The error would be $(0.00136 - 0.00129)/10.0 = 0.0007\%$, which is negligible.

The experimental data on the volume of the final film wetting the inner walls of the pipet after prolonged drainage are given in Table II. These figures indicate that the final film for a 20% sucrose solution is identical with that of water in spite of a kinematic viscosity about 75% greater than that of water. The experimental error here may be about 0.001 ml., which would correspond to a drainage error of 0.006% for a 16-ml. measuring bulb. For a 40% sucrose solution, whose kinematic viscosity is five times that of water, the final film is apparently slightly greater than for water.

TABLE II

FINAL FILM ADHERING TO WALLS OF PIPET AT 25°

Solution	Drainage time, sec.	Density, g./ml.	Weight film, mg.	No. of detns.	Maximum dev., mg.	Av. dev., mg.	Vol. film, ml.
Water	1800	0.99707	11.0	5	3.0	1.0	0.011
20% sucrose	1800	1.07940	12.0	5	6.0	1.0	.011
40% sucrose	1800	1.17439	22.0	3	6.0	2.0	.019
1.43 *M* $Ca_2Fe(CN)_6$	4000	1.2853	18.0	2	3.0	2.0	.014

These data make it very probable that the error due to incomplete drainage in a viscosity measurement with our viscometers would not exceed 0.01% for a 20% sucrose solution and not more than 0.08% for a 40% sucrose solution. Since very few salt solutions even if quite concentrated will have a kinematic viscosity as high as a 20% sucrose solution, we may infer that incomplete drainage is not a serious source of error in the measurement of relative viscosity with the instruments of the Ostwald type used in this Laboratory. It would, of course, be more troublesome in absolute measurements of pure water or other liquids. If an attempt were made to determine the absolute viscosity of water with a measuring bulb of the size and shape which we have used, the error might amount to 0.1% unless due consideration were given to the incomplete drainage. This error might be reduced by using larger bulbs. The results also show with a measuring bulb of 16 ml. and a time of outflow of seven minutes that the after-drainage is small compared to the final film and it may, therefore, be inferred that there is little advantage in providing, as has been suggested in the literature, another bulb above the measuring bulb which resembles the measuring bulb in size and shape in order to provide drainage into the measuring bulb after the meniscus has left the upper mark but before it passes the lower mark.

Summary

1. A form of apparatus is described which is suitable for measuring the drainage of liquids in viscometers and pipets as a function of the time of outflow, the shape and size of the glass surface and the properties of the liquid.

2. It is shown that for a given surface the volume of after-drainage multiplied by the time of outflow is a constant, and that this constant is proportional to the kinematic viscosity of the liquid.

3. It is shown that incomplete drainage is not a serious source of error in the determination of the viscosity of aqueous solutions relative to that of pure water.

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