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Remote Control Viscometer

E. L. CUSSLER AND RAYMOND M. FUOSS
Sterling Chemistry Laboratory, Yale University, New Haven, Connecticut 06520
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A remote control viscometer, designed for use in a high pressure bomb up to 5000 atm, is described. Operation is as follows: a solenoid lifts a tapered piston, which then drops into a cylinder. On the down stroke, needles attached rigidly to the piston dip successively into two mercury wells, the first one starting an electric timer and the second stopping it. Three insulated leads into the bomb are required; the case acts as the common ground. Relative viscosities can be reliably measured within 2%. Results at 30° are given over the pressure range for *n*-propyl ether, cumene, *n*-butyl chloride, and 1,2-dichloroethane.

A NECESSARY supplement to our study of the conductance under pressure of electrolytes in nonaqueous solvents is measurement of the dependence of their viscosities on pressure. A variety of remote control viscometers have already been described[1] but none seemed readily adaptable to the geometry of our high pressure bomb, which pressurizes a cylindrical volume 30.5 cm high and 3.8 cm in diameter.[2] The falling cylinder viscometer[3–5] appeared to be the most promising, provided it could be made to operate by remote control, through the three insulated leads into the bomb. We present here the design of a viscometer in which a tapered piston falls into a cylindrical barrel, starting and stopping an external clock during its fall by means of internal mercury switches attached to the piston. For successive drops, the piston is raised to the starting position by an internal solenoid, which lifts a permanent magnet to which the piston and mercurcy contact needles are attached. A wide range of viscosities can be covered by using pistons of various diameters in a barrel of fixed diameter.

It was found that the drop time is accurately proportional to the viscosity of the liquid in which the assembly is immersed, if a small buoyancy correction is made. Furthermore, the ratio of drop time in a given liquid at pressure p to the drop time in the same liquid at 1 atm is equal to the corresponding relative viscosity, multiplied by the buoyancy factor and another small factor which corrects for the compression of the mercury in the switch tubes. Our values for the relative viscosities of diethyl ether and of isopropanol agree with Bridgman's values[6] to better than 1% up to 5000 atm (our high pressure limit).

VISCOMETER DESIGN

The viscometer will be described in three stages: first, a functional description of the parts and of the assembled instrument; second, a shop description with dimensions and tolerances; and third, a description of assembly and use.

The parts are shown in Fig. 1; assembly is from left to right. The valve block, barrel and mercury tubes are shown in detail in Fig. 2. The tapered piston A1 screws into a flange A2 which also carries a permanent bar magnet A3 and three tungsten wires A4, 5, 6. The piston drops into the barrel B1 (M, Fig. 2), which is filled with the test liquid (because the entire assembly is immersed in the liquid). The time of fall is a measure of the viscosity and is determined by the following sequence of events: the longest tungsten wire A5 makes permanent contact with the mercury in tube B2 (N of Fig. 2); when the assembly A drops, wire A6 first makes contact with mercury in tube B3, starting the timer, and then, before the piston bottoms in the barrel, wire A4 makes contact with mercury in tube B4, stopping the time clock. The barrel and mercury tubes are carried by the valve block, P of Fig. 2, which will be described later. Tubes B3 and B4 are insulated from the valve block by Teflon washers and sleeves; tube B2 fits directly into the block and is the ground lead, because the valve block connects through a series of metal-to-metal contacts with the high pressure bomb. The ball valve P4 in the block closes on the down stroke and opens when the piston is lifted, permitting the barrel to refill with liquid through the channels shown as dotted lines at P2, Fig. 2. The piston assembly is lifted by the solenoid C1, which is wound on a stainless steel bobbin C2. The latter is held in the slotted solenoid housing E by the lock nut D. After the solenoid is inserted in the housing and locked against the flange E1 at the top, the CDE assembly is slipped over the AB assembly, where

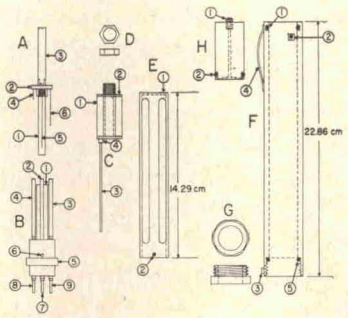

FIG. 1. Piston-cylinder viscometer, exploded view.

[1] J. R. Van Wazer, J. W. Lyons, K. Y. Kim, and R. E. Colewell, *Viscosity and Flow Measurement* (John Wiley & Sons, Inc., New York, 1963). An extensive bibliography on viscometers is also given by R. A. Horne and D. S. Johnson, J. Phys. Chem. **70**, 2183 (1966).
[2] J. F. Skinner and R. M. Fuoss, J. Phys. Chem. **69**, 1437 (1965).
[3] F. Lawaczek, Z. Ver. Deut. Ing. **63**, 677 (1919).
[4] J. J. Bickermann, J. Colloid Sci. **3**, 75 (1948).
[5] T. L. Smith, J. D. Ferry, and F. W. Schremp, J. Appl. Phys. **20**, 144 (1949).
[6] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **61**, 57 (1926).

it rests on the ring B5 of the valve block. It is fixed in position by a small screw E2, which fits into the tapped hole B6. One end of the solenoid winding is soldered to the bobbin and hence is grounded through E; the other end goes to the needle C3 held in an insulated bushing C4. This wire dips into a mercury tube diametrically opposite to tube B2 (and hence invisible in Fig. 1). This tube connects to the stud B7 (Q of Fig. 2) which makes contact with the mercury in tube N through the tie rod S shown in Fig. 2. Tubes B3 and B4 connect with studs B9 and B8 in a similar fashion.

For use, the piston-barrel-solenoid assembly ABCDE is inserted into the outer casing F and locked in by the bottom closure nut G; the O-ring F5, which rests on the ring B5, seals the test liquid from the pressurizing fluid in the bomb. The viscometer is next filled (under vacuum) with the liquid whose viscosity is to be measured. The piston H is inserted into the top of F; the O-rings H2 and F1, and the screw H1 seal the viscometer assembly at the top; pressure is transmitted through the piston H. The entire unit is lowered into the bomb by a cylindrical tool which hooks onto studs F2 (one shown) at the top of the outer casing. The stud F3 fits into a slot in the viscometer support in the bomb, which guides the contacts B7, 8, 9 into three mercury cups on the bottom closure of the bomb. Insulated leads from the mercury cups go through the closure to the external circuits.

The parts shown in Figs. 1 and 2 will now be described in detail, starting with the valve block, B in Fig. 1 and P in Fig. 2. It is made from a piece of stainless steel (alloy 304), 3.016 cm diam and 3.175 cm long, which is turned down to 2.223 cm on each end, to leave a ring 0.635 cm thick 0.953 from the bottom, B5 and P1. Figure 2(b) shows the final cross section of the valve block through the ring. Two 0.3175 cm holes (b1 and b2) at 120° to each other are drilled radially and then plugged (with shrink-fit pins) to a depth of 0.48 cm to form the bottom of the U-tube P2. The ends of this horizontal V-tube connect with the vertical holes at 4 and 8 o'clock shown in Fig. 2(a), and with the hole in the center of the block, P3. The center hole is drilled and tapped to take the cylindrical barrel M into which the piston drops. The center hole has a conical (60°) valve seat, on which a ball bearing P4 (0.476 cm diam) rests. The barrel (5.385 cm long, 1.111 cm o.d., 0.635 cm i.d.) screws into the block. In operation, on the up-stroke when the solenoid C lifts the piston assembly A, liquid is drawn in through the vertical holes and the V-tube, past the ball valve, to fill the barrel. The ball then drops by gravity, closing the bottom exit, and when the piston drops, liquid can only flow up through the annular space between it and the barrel. (This valve is essential; a solenoid will pull a piston from a closed-end barrel, but the long time and large current needed produce far too much heat. With the ball valve, the piston can be lifted without appreciable heating, as shown by exact agreement between drop-times taken at 3 min intervals with those taken at 5 sec intervals.)

The other four holes shown in the top view, Fig. 2(a), are for electrical leads. The one at 12 o'clock is 0.635 cm deep; it receives a stainless steel tube, 5.398 cm long 0.3175 cm o.d., and 0.032 cm wall thickness, which is partly filled with mercury. This is the ground tube; the longest needle A5 dips into it, and thereby connects the flange A2 electrically to the outer casing (F, Fig. 1), which in turn makes electrical contact with the high pressure bomb through the leaf spring contact F4 shown at the top of the outer casing. The holes (0.3175 cm diam) at 2, 6 and 10 o'clock go the whole way through the valve block, as shown in sections a, b, c of Fig. 2. Through them pass the three contact assemblies, shown at the left in Fig. 2. Stainless steel tubes, N (4.763 cm long, 0.318 cm o.d., 0.032 cm wall), are pressed onto threaded studs, R, which receive the 3.81 cm long, 0.159 cm diam rods S, which pass through Teflon tubes in the valve block. The bottom ends of the rods screw into the longer studs Q, which are shown projecting below the valve block (B 7,8,9). Teflon washers, T, at top and bottom, between the corresponding studs and the block, together with the Teflon tubes in the vertical holes, insulate these three mercury tubes from the rest of the viscometer. The lower studs dip into mercury cups, carried on ceramic-insulated nickel wires[2] which pass through the bottom closure of the bomb. The tube at 6 o'clock receives the contact needle C3 from solenoid. The tube at 10 o'clock, (start tube) receives the medium length needle A6 carried by the flange A2; when the needle makes contact with the mercury in this tube, a relay is activated, which starts the timing clock. The tube at 2 o'clock (stop tube) receives the shortest needle A4 (i.e., the last one to make contact when the piston drops); it activates the relay which opens the timing circuit.

The flange A2 is turned from a piece of stainless steel 0.953 cm diam and 1.588 cm long. Cups are turned on top and bottom as shown. Into the top one is pressed the stud on the end of an Alnico bar magnet A3 (5.08 cm long, 0.635 cm diam), ground to a smooth finish. The bottom one is threaded to receive the stud on the top of the piston A1. Two interchangeable pistons, both 5.08 cm long, were used in this work. The one used for isopropanol measurements had a top diameter of 0.6248

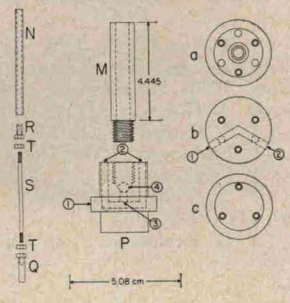

FIG. 2. Mercury tubes, cylinder, and valve block.

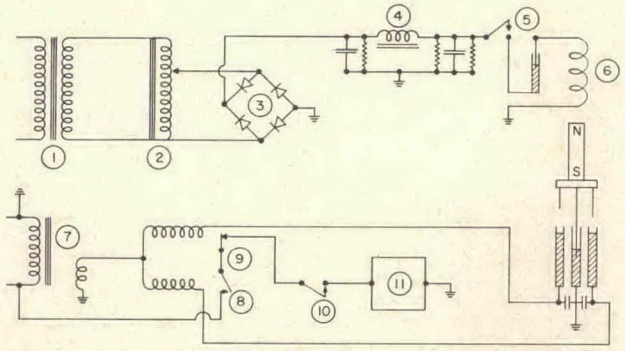

FIG. 3. Wiring diagram for remote control. 1—Isolating transformer; 2—Variac set at about 35 V; 3—full wave rectifier; 4—0.8 H choke; 5—normally open microswitch; 6—solenoid; 7—6.3 V transformer; 8—start-relay contact; 9—stop-relay contact; 10—normally closed microswitch; 11—clock.

cm and a bottom diameter of 0.6172 cm. The one used for ether measurements had a top diameter of 0.6287 cm and a bottom diameter of 0.6210 cm. The bottom edges of both pistons were gently rounded. The taper of 0.1% in the piston is essential; it provides a radial force which keeps the piston centered during its fall. Drop times with cylindrical pistons were hopelessly erratic. Three holes were drilled into the flange A2, on a radius of 0.873 cm to coincide with the centers of the holes at 10, 12 and 2 o'clock in the valve block. Tungsten rods, to project 3.175, 5.080 and 0.953 cm below the flange, ground to 0.064 cm diam were pressed into the holes in the flange. The rods had rounded ends. On assembly, the longest one is centered in the ground tube; the other two will drop into the start and stop tubes, B3 and B4.

The solenoid consists of 800 turns of 26 gauge Teflon insulated magnet wire (resistance 12 Ω), wound on the stainless steel spool C2. The hole through the center is 0.7938 cm diam, and gives ample clearance for the 0.635 cm magnet, so that the viscous drag here is negligible compared to that between piston and barrel. Successive layers of the solenoid windings are separated by Mylar film (0.008 cm). One end of the solenoid winding is hard-soldered to the spool and thereby grounded. The other end is soldered to a 7.62 cm long needle C3 carried by the lower flange of the spool and insulated from the latter by a Teflon bushing. This needle dips into the 6 o'clock tube; an external switch and power source (Fig. 3) complete the solenoid circuit. Power for the solenoid is from a full-wave rectifier (Fig. 3-3), set at about 35 V from the Variac (Fig. 3-2) which is across the output of an isolating transformer. A ballast load of 1000 Ω is across the rectifier output. Ripple is reduced by the 0.8 H choke and the 200 μF condensers and 0.15 MΩ resistors from choke to ground.

The solenoid fits into a stainless steel casing (E, Fig. 1), 14.288 cm long, and 2.54 cm o.d. Four long axial slots are milled into the casing. This casing fits snugly (tolerance 0.0025 cm) around the top of the valve block, resting on the ring B5 of the latter. A small countersunk screw E2 at the bottom of the casing positions the latter reproducibly with respect to the block. The solenoid spool is held to the casing by a nut D at the top; this nut locks the solenoid so that its needle is accurately centered in the 6 o'clock tube when the casing is locked to the block by the screw mentioned above.

The outer casing (F, Fig. 1) is a stainless steel tube 22.86 cm long, 2.540 cm i.d. and 3.493 cm o.d. The shoulder at the bottom is pressed against an O-ring of 2.543 cm i.d. and 0.159 cm thickness by the closure nut; the O-ring F1 is the one which rests on the top of the ring B5 on the valve block, and encircles the solenoid casing. At the top of the outer casing are two spacers, F2, 120° apart, of length equal to the distance between the outer casing and the inside wall of the bomb. At the third 120° position on the top circumference is located a leaf spring F4 which presses the unit into good electrical contact with the bomb. The spacers also serve as lifting pins: a tube with appropriately located L-shaped slots can be fitted around the spacers and is the tool for lowering the viscometer into the bomb and for lifting it out after a run. There is also a pin F3 at the bottom of the outer casing, which fits into a slot in the support for the viscometer in the bomb. This support is a sleeve with a shoulder on which the viscometer rests; the support in turn rests on the bottom closure of the bomb. The outer casing is reproducibly positioned in the bomb by means of the sleeve and the pin at the bottom, and by the spacers F2 and leaf spring F4 at the top. The solenoid casing fits inside the outer casing with only 0.0025 cm clearance, and the valve block fits into the solenoid casing to the same tolerance. In this way, the viscometer is always located in the same position, an essential specification for an instrument which functions through the force of gravity.

The top closure of the viscometer is the piston shown as H, in Fig. 1. Its diameter is 2.535 cm, length 5.08 cm. The seal between the test liquid and the pressurizing fluid is made by two O-rings, H2 and F1, one of which fits into a groove in the piston and the other into a groove in the outer casing, as shown in Fig. 1. After the viscometer is filled, the piston is inserted and sealed with the fillister screw H1.

ASSEMBLY AND USE

Due to the small clearance between piston and barrel, and to the presence of the ball valve, it is essential that all parts of the viscometer be completely dust-free. After rinsing with alcohol and wiping with a lint-free cloth, the barrel and mercury tubes are attached to the valve block and the valve ball is dropped in. Since the fall time depends on the distance traversed by the piston between the times of contact by the start switch and the stop switch, and also on the total length of the piston within the annulus between it and the barrel, it is necessary to

have the levels of the mercury in the start and stop tubes at the same height with respect to the top of the barrel in successive runs. It is also convenient to have these levels equal to each other. The stop and start tubes are filled with mercury to heights 0.100±0.012 cm below the top of the barrel. (This distance is sufficient to avoid mercury overflow when the tungsten wires enter.) About 10 drops of mercury are placed in each tube and then the unit is placed in a chamber which is evacuated. Successive portions of mercury are added, evacuating between portions, until the levels come near the top. (Evacuation is necessary to eliminate trapped air in the mercury tubes.) The final adjustment of levels in the stop and start tubes is made using a Greist microheight gauge and an ohmmeter. The gauge carries a needle which shorts the meter when it just touches the mercury surface.

Then the flange A2 carrying piston, needles and magnet is inserted, and the solenoid housing, carrying the solenoid, is slipped over the valve block and locked into place. An O-ring is placed on the ring of the valve block, and the viscometer is inserted into the outer casing. It is aligned so that the solenoid lead is directly behind the pin in the bottom of the outer casing, and then locked there by the bottom closure nut.

The assembled viscometer is now filled with the test liquid. Entrapped air and suspended dust must be avoided. The viscometer is placed in a chamber under a funnel with a sintered glass frit and a Teflon barrel stopcock. The chamber is evacuated, and then the stopcock is opened, allowing atmospheric pressure to drive the liquid into the viscometer through the filter. When full, the viscometer is removed from the vacuum chamber and the top closure piston is inserted. The latter is pushed down until liquid flows through the central channel, which is then sealed with the fillister screw. Finally, the entire assembly is lowered into the high pressure bomb and rotated until the pin at the bottom of the outer casing engages a slot in the cell support. In this position, the three studs at the bottom automatically go into the appropriate mercury cups in the bottom closure of the bomb, completing the electrical control circuit shown in Fig. 3. To prevent sparking, 0.1 μF condensers connect the start and stop tubes to ground.

The bomb is held at 30.0±0.1° by water which circulates through 1.27 cm i.d. copper tubing wrapped around it. The tubing is cemented to the bomb with Thermon T-85,[7] which has good thermal conductivity. The assembly is thermally insulated from the room by aluminum foil and rock wool.

After temperature equilibrium is reached (about 30 min), a series of drop times at 1 atm is taken. The normally closed microswitch in the clock line is opened and the solenoid switch (normally open microswitch) is closed for about $\frac{1}{2}$ sec. This raises the piston, without starting the clock on the up-stroke. The switches are released; when the long needle touches its mercury well, the normally open relay closes and starts the clock. When the short needle contacts, the normally closed relay opens, stopping the clock. For fall times less than 5 sec, 30 readings are taken and averaged; for less than 60 sec, 12 readings; and for more than 60 sec, 8 readings. Then drop times are determined at higher pressures, usually at intervals of 700 kg cm^{-2} gauge. Pressure increase should be gradual, at not more than about 35 kg cm^{-2} min^{-1}, in order to allow the heat of compression to dissipate. Too rapid compression sets up troublesome thermal gradients in the viscometer, and in extreme cases has caused the piston to seize in the barrel.

[7] Obtained from the Lars Anderson Co., So. Weymouth, Mass.

TABLE I. Determination of viscometer constant A'.

Liquid	100η	$(1-\rho v/w)$	t (sec)	A'
Isopropanol	1.765	0.897	5.00	254
Ethanol	1.003	0.897	2.78	249
Ethylene dichloride	0.730	0.836	2.23	255
o-xylene	0.709	0.885	2.00	250
n-butyl chloride	0.405	0.885	1.20	262
Cumene	0.725	0.887	2.07	253
Carbon tetrachloride	0.845	0.792	2.73	256
n-propyl ether	0.376	0.902	1.10	264

EXPERIMENTAL RESULTS

The drop time t of the piston-cylinder viscometer is given by the equation[5]

$$t=A\eta(h_2^2-h_1^2)/(1-\rho v/w) \qquad (1)$$

where A is an instrument constant, ρ is the density of the liquid, η is its viscosity, v is the volume of the falling piston plus attached parts, w their weight, and h_2 and h_1, are, respectively, the distance from the top of the cylinder to the bottom of the piston at the stop and start of the timing period $t=t_2-t_1$. For a given piston and cylinder, with h_2 and h_1 fixed,

$$t=A'\eta/(1-\rho v/w). \qquad (2)$$

For our apparatus, $v/w=0.132_3$ cc/g.

Our first test of the reproducibility of the viscometer was the determination with the piston later used for isopropanol experiments of drop times at atmospheric pressure and 30° in eight liquids of known viscosity and density. The results are summarized in Table I.

The values of the constant average to 255±5. The uncertainty of about 3% is less than half that observed by Bridgman with the falling weight viscometer.[6] It should be mentioned that the viscometer was completely disassembled between runs for cleaning; the ±3% probably is mostly due to slight differences in setting the mercury heights (which enter as the square in the viscometer equation).

The viscometer was then tested at various pressures up to about 5000 atm with isopropanol and diethyl ether.

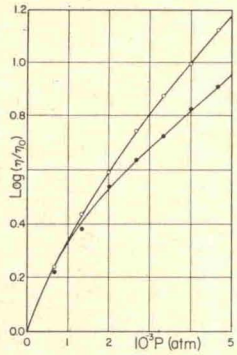

FIG. 4. Relative viscosity as function of pressure. Open circles—isopropanol; solid circles—diethyl ether; curves—Bridgman's results.[6]

Since density depends on pressure, and density appears in the buoyancy factor of Eq. (1), density of the test liquid as a function of pressure must be known; we used Bridgman's values.[8] Also, since mercury is compressible, the factor $(h_2^2-h_1^2)$ in Eq. (1) will vary with pressure. Since we are interested in relative viscosities, the pressure-independent[9] instrument constant A divides out and the relevant viscometer equation becomes

$$\frac{\eta}{\eta_0}=\frac{t}{t_0}\frac{1-\rho v/w}{1-p_0 v/w}\frac{(h_2^2-h_1^2)_0}{h_2^2-h_1^2} \tag{3}$$

where the subscript zero indicates values at 1 atm. The last factor in Eq. (3) can be considerably simplified, because

$$h=h_0(1-\beta P/3) \tag{4}$$

where β is the compressibility of mercury.[10] Inserting this factor, we have to a close approximation

$$\eta/\eta_0=(t/t_0)(1-\rho v/w)/(1-2\beta P/3)(1-\rho_0 v/w). \tag{5}$$

The results are shown in Fig. 4, where the smooth curves are drawn through Bridgman's values. Our data are based on three runs for each liquid (viscometer emptied, cleaned and reassembled between each run). The circles in Fig. 4 represent the average of the three determinations at each pressure; the average scatter at fixed pressure was within 0.2% for diethyl ether and within 0.4% for isopropanol, with a tendency to increase towards the high pressure end of the scale. The agreement with Bridgman's values is excellent except for diethyl ether at 700 and 1400 kg cm^{-2}, where our results are about 6% higher. Faust[11] reports values of η/η_0 which are 20% higher than Bridgman's in this pressure range. Except for this unexplained discrepancy, the performance of the viscometer over a wide range of pressures and viscosities has been entirely satisfactory; the present precision of about 2% in relative viscosity can probably be improved by a more accurate clock and by better pressure gauges. A bellows for the top closure of the outer casing instead of the present piston is planned; this will permit more convenient assembly and will eliminate the two top O-rings, leaving only the one at the bottom closure to be exposed to the test liquid.

Once the viscometer reached temperature equilibrium in the bomb, drop times at a given pressure were usually reproducible within about 0.03 sec. Occasionally an erratic result would appear, presumably due to a speck of dust: the drop time would be too short if a dust particle were caught between the ball valve and its seat, and too long if it were in the annulus between piston and barrel. After a pressure run, the 1 atm drop time was rechecked; no hysteresis was observed. (If the O-rings leaked, pressurizing fluid would enter the viscometer and obviously would change the drop time.) In order to test the reproducibility of positioning the viscometer in the bomb, a number of repeat runs on the same liquid were made, the viscometer was taken apart, rinsed, dried, refilled and reassembled between runs. Typical results at 30° for four liquids are summarized in Table II, where each line represents a single run. Relative viscosities are given under the pressures (kg cm^{-2}) in the last seven columns. The first column gives the drop times (sec) at 1 atm. The average precision is about 2.0%.

TABLE II. Relative viscosities at 30°.

	703 kg cm^{-2}	1406	2110	2810	3515	4220	4920
				n-propyl ether			
t							
1.11 sec	1.76	2.62	3.82	5.38	7.22	9.57	12.5
1.09	1.73	2.61	3.66	5.23	7.13	9.30	12.3
				Cumene			
2.28	1.62	2.52	3.86	6.03	9.15	13.0	18.9
2.21	1.57	2.48	3.90	6.27	9.05	12.8	19.2
				1, 2-dichloroethane			
2.23	1.47	2.09	2.87	3.98	...	...	...
2.22	1.51	2.10	2.99	4.02	...	...	...
				n-butyl chloride			
1.34	1.54	2.19	3.07	4.22	5.69	7.26	9.23
1.40	1.57	2.16	2.96	4.22	5.65	7.17	9.04

ACKNOWLEDGMENT

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[8] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **49**, 1 (1913).

[9] The constant A includes the annular spacing between piston and cylinder and in fact does change with pressure. But the compressibility of stainless steel is so small that the error in assuming $\partial A/\partial p=0$ is negligible.

[10] L. A. Davis and R. B. Gordon, J. Chem. Phys. **46**, 2650 (1967).

[11] O. Faust, Z. Phys. Chem. **86**, 479 (1914).