



FIG. 4. Relative viscosity as function of pressure. Open circles—*isopropanol*; solid circles—*diethyl ether*; curves—*Bridgman's results*.<sup>6</sup>

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.<sup>8</sup> 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<sup>9</sup> instrument constant  $A$  divides out and the relevant viscometer equation becomes

$$\frac{\eta}{\eta_0} = \frac{t}{t_0} \frac{1 - \rho v/w}{1 - \rho_0 v/w} \frac{(h_2^2 - h_1^2)_0}{h_2^2 - h_1^2} \quad (3)$$

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

$$h = h_0(1 - \beta P/3) \quad (4)$$

where  $\beta$  is the compressibility of mercury.<sup>10</sup> Inserting this

TABLE II. Relative viscosities at 30°.

	703 kg cm <sup>-2</sup>	1406	2110	2810	3515	4220	4920
<i>n</i> -propyl ether							
<i>t</i>							
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	...	...	...
<i>n</i> -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

<sup>8</sup> P. W. Bridgman, *Proc. Am. Acad. Arts Sci.* **49**, 1 (1913).

<sup>9</sup> 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.

<sup>10</sup> L. A. Davis and R. B. Gordon, *J. Chem. Phys.* **46**, 2650 (1967).

factor, we have to a close approximation

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

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<sup>-2</sup>, where our results are about 6% higher. Faust<sup>11</sup> reports values of  $\eta/\eta_0$  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<sup>-2</sup>) in the last seven columns. The first column gives the drop times (sec) at 1 atm. The average precision is about 2.0%.

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<sup>11</sup> O. Faust, *Z. Phys. Chem.* **86**, 479 (1914).