concentric cylinder viscometer, an extrapolation of the curve in Fig. 1 over an interval of merely 27°C is quite easy and reliable. From an enlargement of this figure we thus estimate $\eta = 10^{13.2}$ poises at 240°.

In the case of glucose glass the transition region centers around 25°C and the viscosity study[5] previously referred to yielded a value of $10^{13.1}$ poises at this temperature. A more recent, unpublished investigation in this laboratory also gives values ranging from $10^{13.2}$ to $10^{14.1}$ poises at 25°, depending on the extent of the annealing and previous working of some glassy glucose fibers. Moreover, some viscosity studies on commercial inorganic glasses[5] have yielded values in the neighborhood of $10^{13.7}$ poises for this transition region.

It thus appears that the *transition region* in glass-forming materials, whether these be inorganic or organic in character, or composed of only one component or of several components, can be in general identified with a viscosity of the order of 10^{13} to 10^{14} poises. This rule, while purely empirical at present, should be very useful in the study of amorphous solids.

[5] W. E. S. Turner, *The Constitution of Glass*, The Society of Glass Technology, Sheffield, England (1927), pp. 73 and 160. See also Samsoen, Comptes rendus **182**, 517 (1926).

The Viscosity of Mixtures of Liquids at High Pressures[1]

R. B. Dow, *Research Laboratory of Physics, Harvard University*

The effects of pressure and temperature change on the viscosity of organic, binary mixtures have been investigated by methods developed and used by P. W. Bridgman. Six mixtures have been examined over the entire concentration range at two temperatures, 30° and 75°C, and at pressures extending to 12,000 kg/cm². The isobaric, log viscosity-concentration curves for *n*-hexane carbon disulphide, and *n*-hexane *n*-decane are linear at both temperatures, indicating that these mixtures obey Arrhenius' empirical equation for the viscosity of a binary mixture. It is believed that a comparatively simple type of interlocking among molecules occurs in these mixtures due to the effectively linear structure of the molecules and the absence of non-uniform molecular fields such as would cause some sort of association. For the remaining mixtures: *n*-hexane diethyl ether, *n*-hexane chlorobenzene, *n*-pentane benzene, and eugenol carbon disulphide, the corresponding viscosity isobars are more complex; irregularities occur in certain regions of concentration which vary with temperature and pressure. In these latter mixtures, the interlocking at high pressures is complicated by the structural differences of the component molecules and their effects. The viscosity of *n*-decane as a function of pressure and temperature has also been investigated. Density data at atmospheric pressure and 30° are included in the paper.

TO study the effect of hydrostatic pressure on the viscosity of pure liquids, P. W. Bridgman[2] investigated forty-three pure liquids through a pressure range of 12,000 kg/cm² at 30° and 75°C. His data indicate that viscosity at high pressures is entirely different from that at ordinary conditions and that the "free-space" between molecules is largely decreased, crowding the molecules together in such a way that some sort of interlocking takes place. This conception gives a possible reason for the great increase in viscosity at high pressures.

It becomes interesting to extend such measurements of viscosity at high pressures to include mixtures of liquids for it is obvious that with different kinds of molecules in mixture the interlocking can be studied more completely than for pure liquids, since it is believed that the degree of interlocking depends on the size and shape of molecules. Consequently, this paper is devoted to the effects of various pressures and temperatures on the viscosity of six liquid, organic mixtures. With the exception of *n*-decane, the pure liquids used for the mixtures have been

studied by Bridgman.[2] The viscosity of *n*-decane at 30° and 75°C through a pressure range of 6000 kg/cm² is included in this investigation. In addition to the viscosity measurements, the density-concentration data at 30°C and atmospheric pressure are recorded for completeness.

METHOD AND EXPERIMENTAL PROCEDURE

The method of preparing the mixtures was comparatively simple. The volume of each liquid was determined by a calibrated pipette which discharged between two graduations, and immediately after mixing, the density of the mixture at 30° was determined by a calibrated pycnometer which was fitted with ground glass caps to prevent evaporation.

The method employed in the viscosity measurements was that of Bridgman.[2] As the viscometer has been described previously,[2, 3, 4] it will suffice to recall the essentials of the instrument for the reader. It is of the falling-weight type consisting of a small cylindrical weight which is allowed to fall a few centimeters in a hollow steel cylinder of slightly larger internal diameter, the time of fall being measured electrically with a suitable timing device. In this way, the relative viscosity is measured by the time of fall. The time of fall could be found in opposite directions by enclosing the viscometer in a specially shaped pressure chamber which was connected to the remainder of the pressure apparatus in such a way that the whole assembly could be rotated through 180° by hand.

The pressure apparatus was of the type commonly used by Bridgman[3] in his investigations at high pressures, and was set up horizontally so that the viscometer could be rotated in a simple way. The pressures were determined as previously in this laboratory by measuring the changes of resistance of a manganin coil that was connected in the high pressure side of the press. The pressure chamber that contained the viscometer was surrounded by a constant temperature bath of water, the temperature being read on a corrected thermometer.

[3] P. W. Bridgman, *Physics of High Pressure*, Chap. 12, The Macmillan Co. (1931).
[4] E. Hatschek, *Viscosity of Liquids*, Chap. 6, Blackie and Sons (1928).

TABLE I. *Densities,* ζ *(in g/cm³) of mixtures of varying concentrations (in mole percent).*

Conc.	Dens.	Conc.	Dens.	Conc.	Dens.	Conc.	Dens.
1. *n*-HEXANE CARBON DISULPHIDE		2. *n*-HEXANE DIETHYL ETHER		4. *n*-HEXANE CHLORO-BENZENE		5. *n*-PENTANE BENZENE	
31.8	0.959	0.0	0.701	49.0	0.851	43.8	0.748
58.2	0.802	33.1	0.682	75.5	0.975	11.5	0.837
41.1	0.890	28.3	0.685	34.0	0.787	66.2	0.693
20.2	1.043	35.4	0.679	63.0	0.914	82.4	0.657
13.4	1.110	41.8	0.673	100.0	1.098	28.0	0.787
4.9	1.190	79.8	0.662	88.4	1.042	52.3	0.725
0.0	1.244	49.7	0.673	17.6	0.722	75.1	0.672
82.9	0.702	16.5	0.692	94.6	1.074	100.0	0.617
46.4	0.856	75.5	0.662	5.1	0.678	0.0	0.869
41.1	0.890	84.1	0.659	1.8	0.667	59.2	0.707
73.5	0.738	3. *n*-HEXANE *n*-DECANE		97.3	1.087	36.2	0.765
65.1	0.771			90.0	1.050	19.8	0.809
54.7	0.816	40.1	0.687	69.6	0.945	55.6	0.716
100.0	0.654	100.0	0.727	87.4	1.036		
		70.0	0.707	92.8	1.062	6. EUGENOL CARBON DISULPHIDE	
2. *n*-HEXANE DIETHYL ETHER		28.6	0.680	96.4	1.082		
		59.2	0.700			10.5	1.194
44.2	0.671	85.7	0.717	91.5	1.056	28.2	1.143
70.2	0.658	50.4	0.694	9.9	0.692	54.1	1.097
20.8	0.689	19.7	0.673	3.5	0.670	20.8	1.161
29.8	0.684	4.6	0.663	13.0	0.706	43.9	1.116
34.6	0.680	13.5	0.670	7.6	0.684	52.0	1.100
55.9	0.668	94.1	0.723	9.0	0.690	0.0	1.244
88.8	0.656	77.0	0.712	95.0	1.076	69.2	1.078
10.2	0.698	0.0	0.660	80.0	0.998	86.8	1.062
100.0	0.654			3.0	0.669	33.9	1.130
				11.5	0.700	5.1	1.219
				0.0	0.660	80.0	1.067

DATA

The following six mixtures were studied through the entire range of concentration: *n*-hexane carbon disulphide, *n*-hexane diethyl ether, *n*-hexane *n*-decane, *n*-hexane chlorobenzene, *n*-pentane benzene, and eugenol carbon disulphide. Most of the liquids were of the best grade of Eastman and some were further purified by redistilling. Table I is a summary of the density data obtained as results of the pycnometer measurements.

The measured quantities for a viscosity determination were time of fall, pressure and temperature. The viscosity was computed from the time of fall by applying correction formulas[2] for the various errors caused by pressure effects. Following Bridgman, the common logarithm of the viscosity, instead of the viscosity itself, is given because of the very rapid increase of viscosity with increase of pressure. The viscosity of each mixture at atmospheric pressure at 30° was taken as unity, and the relative viscosity computed from $\log_{10} t/t_0$, t being the corrected time of fall at a certain pressure and temperature, and t_0 the time of fall at atmospheric pressure at 30°. The values of $\log_{10} t/t_0$ at 30° and 75°,

varying

. Dens.
-PENTANE
¿NZENE
8 0.748
5 0.837
2 0.693
4 0.657
0 0.787
3 0.725
1 0.672
0 0.617
0 0.869
2 0.707
2 0.765
8 0.809
6 0.716
EUGENOL
¿ARBON
¿ULPHIDE
5 1.194
2 1.143
1 1.097
8 1.161
9 1.116
0 1.100
0 1.244
0 1.054
2 1.078
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TABLE II. *Viscosity of n-decane.* Values of $\log t/t_0$ where t_0 is the time of fall at 30°C and atmospheric pressure ($\log t_0 = 0.826$).

Pressure (kg/cm²)	Log t/t_0	
	30°	75°
1	0.000	0.208
500	0.184	0.005
1000	0.356	
2000	0.659	0.359
3000	0.939	0.585
4000	1.212	0.785
6000		1.163

$\log_{10} t_0$,[5] and the pressures in kg/cm² are given in Table II for *n*-decane, and with the molar concentrations in Table III for the six binary mixtures. In the course of these experiments, the viscosities of the pure liquids were redetermined and the values found to be in good agreement with those of Bridgman, the disagreement in any case not amounting to over two percent.

As Table III does not show the interesting and unusual features exhibited by these results, isobaric viscosity-concentration diagrams are given in several instances in order that the significance of the data may be better visualized.

It is difficult to estimate the error in these experiments. The total percentage error estimated for a typical mixture of *n*-hexane chlorobenzene at a pressure of 500 kg/cm² at 30° amounted to about two percent, and increased to three percent at 75°. At higher pressures these errors became less. However, on estimating that part of the error contributed by the data of Table III by considering how well the experimental points fitted a smooth curve, the maximum deviation of a plotted point from the smooth viscosity-pressure curve for the same mixture at 30° corresponded to an error of 0.5 percent in the fall time. The remaining 7 points fitted the curve within the error of drawing. The similar curve at 75° showed that all the points fitted it without any noticeable deviations. Consequently, since the greater part of the total error came from the errors in the quantities of Table III, it is reasonable to expect that the total error amounted to less than that estimated as the percentage error.

[5] The viscometer was not designed for high accuracy in the time of fall, t_0 at atmospheric pressure; hence these values should be used with caution in further applications.

DISCUSSION OF RESULTS

(1) Viscosity of *n*-decane at various pressures and temperatures

The viscosity of *n*-pentane, *n*-hexane and *n*-octane of the methane series has been investigated under various pressure and temperature conditions by Bridgman.[2] The data of this paper extend these measurements to include *n*-decane. In general, the pressure coefficient of viscosity, as well as the temperature coefficient, is similar to those of the other paraffins that have been studied. The relation between the logarithm of viscosity and molecular weight is apparently simple for the members of this series at high pressures. By plotting log viscosity against molecular weight for these liquids at 4000 kg/cm² and 30°, it will be found that the points lie on a curve which closely approaches a straight line. Also, at 75° a similar curve at 6000 kg/cm² approaches linearity.

(2) Viscosity-concentration curves at constant pressure, at 30° and 75°

The isobaric viscosity-concentration curves, plotted from the data of Table III, may be conveniently divided into two classes. First, the curves for which the log relative viscosity is a linear function of the molar concentration through the entire pressure range at 30° and 75°, representing the mixtures *n*-hexane carbon disulphide and *n*-hexane *n*-decane, Figs. 1 and 2, the curves at 75° being omitted as they are qualitatively similar. Secondly, the curves of the remaining mixtures under similar conditions for which the log relative viscosity varies in a complicated way with the molar concentration, Figs. 3 to 9 inclusive.

The components of the mixtures of the first group are similar in that they are simple nonpolar liquids which would be expected to dissolve in solution without the complications due to non-uniform molecular fields. *A priori*, it might be thought that the tendency of the molecules would be toward an end-to-end arrangement, contributing to an orientation more or less parallel to the lines of flow, the viscosity being the resistance of these parallel layers of molecules

TABLE III. *Viscosity of mixtures as function of concentration and pressure.*

1. n-HEXANE CARBON DISULPHIDE

Pressure (kg/cm²)	31.8 mole % C_6H_{14}, log t_0 = 0.508 — 30°	75°	58.2 mole % C_6H_{14}, log t_0 = 0.470 — 30°	75°
1	0.000	0.103	0.000	0.153
500	0.104	0.003	0.150	0.015
1000	0.202	0.089	0.259	0.102
2000	0.371	0.242	0.447	0.297
4000	0.644	0.471	0.750	0.570
6000	0.849	0.660	0.990	0.785
8000	1.031	0.830	1.226	0.965
10000	1.239	1.015	1.480	1.169

Pressure	13.4 mole % C_6H_{14}, log t_0 = 0.529 — 30°	75°	4.9 mole % C_6H_{14}, log t_0 = 0.537 — 30°	75°
1	0.000	0.141	0.000	0.117
500	0.093	0.041	0.080	0.040
1000	0.165	0.050	0.159	0.031
2000	0.339	0.201	0.304	0.159
4000	0.574	0.444	0.540	0.364
6000	0.740	0.633	0.707	0.528
8000	0.902	0.749	0.880	0.669
10000	1.109	0.900	1.060	0.831

Pressure	20.2 mole % C_6H_{14}, log t_0 = 0.498 — 30°	75°	46.4 mole % C_6H_{14}, log t_0 = 0.470 — 30°	75°
1	0.000	0.117	0.000	0.124
500	0.100	0.024	0.136	0.005
1000	0.195	0.060	0.230	0.100
2000	0.349	0.106	0.425	0.276
4000	0.599	0.427	0.695	0.533
6000	0.791	0.618	0.918	0.732
8000	0.979	0.789	1.140	0.891
10000	1.201	0.831	1.390	1.076

Pressure	41.1 mole % C_6H_{14}, log t_0 = 0.484 — 30°	75°	82.9 mole % C_6H_{14}, log t_0 = 0.452 — 30°	75°
1	0.000	0.132	0.000	0.111
500	0.126	0.024	0.164	0.012
1000	0.226	0.075	0.295	0.125
2000	0.407	0.247	0.520	0.325
4000	0.669	0.499	0.850	0.640
6000	0.900	0.705	1.130	0.885
8000	1.100	0.886	1.398	1.092
10000	1.332	1.057	1.665	1.310

Pressure	73.5 mole % C_6H_{14}, log t_0 = 0.440 — 30°	75°	54.7 mole % C_6H_{14}, log t_0 = 0.465 — 30°	75°
1	0.000	0.158	0.000	0.119
500	0.151	0.000	0.125	0.008
1000	0.279	0.128	0.240	0.097
2000	0.492	0.330	0.440	0.282
4000	0.820	0.610	0.740	0.560
6000	1.080	0.828	0.966	0.775
8000	1.326	1.035	1.198	0.940
10000	1.606	1.258	1.469	1.140

Pressure	65.1 mole % C_6H_{14}, log t_0 = 0.455 — 30°	75°
1	0.000	0.133
500	0.160	0.002
1000	0.239	0.115
2000	0.470	0.310
4000	0.765	0.590
6000	1.036	0.805
8000	1.290	1.000
10000	1.520	1.220

2. n-HEXANE DIETHYL ETHER

Pressure	44.2 mole % C_6H_{14}, log t_0 = 0.362 — 30°	75°	70.2 mole % C_6H_{14}, log t_0 = 0.398 — 30°	75°
1	0.000	0.054	0.000	0.113
500	0.131	0.041	0.139	0.010
1000	0.253	0.130	0.260	0.122
2000	0.470	0.299	0.470	0.319
4000	0.813	0.600	0.795	0.632
6000	1.089	0.860	1.089	0.881
8000	1.341	1.090	1.379	1.091
10000	1.617	1.281	1.677	1.290
12000		1.490		1.490

2. n-HEXANE DIETHYL ETHER—Continued.

Pressure	20.8 mole % C_6H_{14}, log t_0 = 0.352 — 30°	75°	29.8 mole % C_6H_{14}, log t_0 = 0.359 — 30°	75°
1	0.000	0.080	0.000	0.060
500	0.134	0.036	0.118	0.032
1000	0.248	0.141	0.225	0.120
2000	0.442	0.323	0.414	0.280
4000	0.739	0.606	0.721	0.549
6000	0.972	0.822	0.997	0.769
8000	1.210	1.000	1.239	0.959
10000	1.447	1.164	1.475	1.143
12000		1.315		1.330

Pressure	34.6 mole % C_6H_{14}, log t_0 = 0.348 — 30°	75°	55.9 mole % C_6H_{14}, log t_0 = 0.371 — 30°	75°
1	0.000	0.005	0.000	0.110
500	0.132	0.079	0.148	0.005
1000	0.250	0.160	0.273	0.111
2000	0.450	0.311	0.485	0.304
4000	0.752	0.572	0.809	0.609
6000	1.012	0.809	1.095	0.842
8000	1.272	1.015	1.364	1.049
10000	1.529	1.202	1.619	1.261
12000		1.380		1.469

Pressure	88.8 mole % C_6H_{14}, log t_0 = 0.401 — 30°	75°	10.2 mole % C_6H_{14}, log t_0 = 0.324 — 30°	75°
1	0.000	0.109	0.000	0.044
500	0.143	0.022	0.130	0.040
1000	0.275	0.139	0.241	0.121
2000	0.501	0.342	0.431	0.270
4000	0.857	0.639	0.729	0.526
6000	1.165	0.883	0.979	0.743
8000	1.474	1.109	1.210	0.942
10000	1.770	1.330	1.428	1.130
12000		1.550		1.314

Pressure	33.1 mole % C_6H_{14}, log t_0 = 0.349 — 30°	75°	28.3 mole % C_6H_{14}, log t_0 = 0.346 — 30°	75°
1	0.000	0.094	0.000	0.095
500	0.140	0.022	0.141	0.019
1000	0.262	0.129	0.262	0.121
2000	0.469	0.310	0.456	0.305
4000	0.790	0.596	0.739	0.591
6000	1.057	0.825	0.994	0.812
8000	1.306	1.028	1.250	1.009
10000	1.540	1.204	1.506	1.199
12000		1.395		1.389

Pressure	35.4 mole % C_6H_{14}, log t_0 = 0.361 — 30°	75°	41.8 mole % C_6H_{14}, log t_0 = 0.354 — 30°	75°
1	0.000	0.110	0.000	0.090
500	0.129	0.009	0.133	0.012
1000	0.247	0.120	0.253	0.110
2000	0.450	0.313	0.456	0.295
4000	0.771	0.605	0.764	0.601
6000	1.049	0.830	1.055	0.860
8000	1.320	1.039	1.340	1.089
10000	1.601	1.244	1.629	1.300
12000		1.450		1.491

3. n-HEXANE n-DECANE

Pressure	40.1 mole % $C_{10}H_{22}$, log t_0 = 0.580 — 30°	75°	70.0 mole % $C_{10}H_{22}$, log t_0 = 0.716 — 30°	75°
1	0.000	0.175	0.000	0.194
500	0.185	0.016	0.186	0.002
1000	0.342	0.136	0.347	0.098
2000	0.600	0.382	0.633	0.347
3000	0.810	0.554	0.878	0.561
4000	1.021	0.757	1.125	0.765

Pressure	28.6 mole % $C_{10}H_{22}$, log t_0 = 0.520 — 30°	75°	59.2 mole % $C_{10}H_{22}$, log t_0 = 0.657 — 30°	75°
1	0.000	0.159	0.000	0.166
500	0.179	0.001	0.187	0.013
1000	0.331	0.136	0.349	0.135
2000	0.580	0.355	0.620	0.373
3000	0.795	0.549	0.856	0.580
4000	0.992	0.727	1.089	0.767

3. n-HEXANE n-DECANE—Continued.

Pressure	85.7 mole % $C_{10}H_{22}$, log t_0 = 0.768 — 30°	75°	50.4 mole % $C_{10}H_{22}$, log t_0 = 0.631 — 30°	75°
1	0.000	0.196	0.000	0.186
500	0.199	0.016	0.187	0.010
1000	0.362	0.110	0.350	0.120
2000	0.642	0.367	0.620	0.379
3000	0.909	0.585	0.841	0.564
4000	1.170	0.783	1.061	0.758

Pressure	19.7 mole % $C_{10}H_{22}$, log t_0 = 0.503 — 30°	75°	4.6 mole % $C_{10}H_{22}$, log t_0 = 0.420 — 30°	75°
1	0.000	0.151	0.000	0.135
500	0.175	0.010	0.179	0.012
1000	0.328	0.163	0.327	0.140
2000	0.581	0.363	0.563	0.360
3000	0.791	0.549	0.749	0.539
4000	0.970	0.712	0.926	0.705

Pressure	13.5 mole % $C_{10}H_{22}$, log t_0 = 0.462 — 30°	75°	94.1 mole % $C_{10}H_{22}$, log t_0 = 0.801 — 30°	75°
1	0.000	0.137	0.000	0.231
500	0.187	0.017	0.179	0.006
1000	0.336	0.157	0.347	0.103
2000	0.570	0.377	0.650	0.374
3000	0.769	0.557	0.921	0.597
4000	0.954	0.710	1.198	0.781

Pressure	77.0 mole % $C_{10}H_{22}$, log t_0 = 0.731 — 30°	75°
1	0.000	0.204
500	0.181	0.004
1000	0.340	0.115
2000	0.629	0.364
3000	0.876	0.574
4000	1.112	0.767

4. n-HEXANE CHLOROBENZENE

Pressure	49.0 mole % C_6H_5Cl, log t_0 = 0.563 — 30°	75°	75.5 mole % C_6H_5Cl, log t_0 = 0.681 — 30°	75°
1	0.000	0.160	0.000	0.186
500	0.122	0.040	0.131	0.067
1000	0.242	0.075	0.253	0.047
2000	0.466	0.290	0.476	0.251
4000	0.860	0.639	0.860	0.585
6000	1.212	0.921	1.277	0.861
8000	1.530	1.150	1.778	1.147

Pressure	34.0 mole % C_6H_5Cl, log t_0 = 0.509 — 30°	75°	63.0 mole % C_6H_5Cl, log t_0 = 0.628 — 30°	75°
1	0.000	0.145	0.000	0.169
500	0.136	0.010	0.127	0.044
1000	0.260	0.109	0.249	0.072
2000	0.476	0.308	0.460	0.272
4000	0.820	0.600	0.840	0.586
6000	1.137	0.847	1.210	0.831
8000	1.505	1.132	1.590	1.104

Pressure	88.4 mole % C_6H_5Cl, log t_0 = 0.749 — 30°	75°	17.6 mole % C_6H_5Cl, log t_0 = 0.463 — 30°	75°
1	0.000	9.815	0.000	0.174
500	0.117	9.932	0.115	0.026
1000	0.234	0.040	0.230	0.101
2000	0.462	0.234	0.450	0.309
4000	0.900	0.555	0.864	0.608
6000	1.330	0.842	1.257	0.850
8000	1.760	1.170	1.630	1.095

Pressure	94.6 mole % C_6H_5Cl, log t_0 = 0.766 — 30°	75°	5.1 mole % C_6H_5Cl, log t_0 = 0.419 — 30°	75°
1	0.000	9.810	0.000	0.155
500	0.115	9.939	0.141	0.010
1000	0.225	0.025	0.276	0.115
2000	0.439	0.214	0.529	0.325
4000	0.892	0.521	0.960	0.639
6000	1.403	0.809	1.316	0.881
7000	1.701			
8000		1.156	1.965	1.144

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g t/t₀
75°

...ued.

4 mole
C₁₀H₂₂
= 0.631

	75°
0	0.186
7	0.010
0	0.120
0	0.379
1	0.564
1	0.758

.6 mole
C₁₀H₂₂
₀ = 0.420

	75°
0	0.135
9	0.012
7	0.140
3	0.360
9	0.539
6	0.705

.1 mole
C₁₀H₂₂
₀ = 0.801

	75°
0	0.231
79	0.006
47	0.103
50	0.374
21	0.597
98	0.781

...NE

5.5 mole
C₆H₅Cl
t₀ = 0.681

	75°
00	0.186
31	0.067
53	0.047
76	0.251
60	0.585
77	0.861
78	1.147

3.0 mole
% C₆H₅Cl
t₀ = 0.628

	75°
00	0.169
27	0.044
49	0.072
60	0.272
40	0.586
10	0.831
90	1.104

17.6 mole
% C₆H₅Cl
t₀ = 0.463

	75°
00	0.174
15	0.026
30	0.101
50	0.309
64	0.608
57	0.850
30	1.095

5.1 mole
% C₆H₅Cl
t₀ = 0.419

	75°
000	0.155
.141	0.010
.276	0.115
.529	0.325
.960	0.639
.316	0.881
.965	1.144

4. n-HEXANE CHLOROBENZENE—*Continued.* (first main column)

1.8 mole % C₆H₅Cl, log t₀ = 0.405 | 97.3 mole % C₆H₅Cl, log t₀ = 0.773

Pressure (kg/cm²)	30°	75°	30°	75°
1	0.000	0.124	0.000	0.175
500	0.163	0.015	0.124	0.063
1000	0.304	0.135	0.241	0.043
2000	0.547	0.338	0.460	0.233
4000	0.927	0.607	0.847	0.545
6000	1.219	0.895	1.170	0.840
8000	1.504	1.160		1.180

90.0 mole % C₆H₅Cl, log t₀ = 0.765 | 69.6 mole % C₆H₅Cl, log t₀ = 0.664

Pressure	30°	75°	30°	75°
1	0.000	0.217	0.000	0.165
500	0.116	0.095	0.135	0.043
1000	0.227	0.017	0.262	0.072
2000	0.440	0.215	0.496	0.266
4000	0.830	0.529	0.902	0.565
6000	1.226	0.812	1.260	0.830
8000		1.140		1.139

87.4 mole % C₆H₅Cl, log t₀ = 0.730 | 92.8 mole % C₆H₅Cl, log t₀ = 0.756

Pressure	30°	75°	30°	75°
1	0.000	0.180	0.000	0.179
500	0.115	0.060	0.114	0.069
1000	0.222	0.049	0.225	0.033
2000	0.421	0.231	0.441	0.221
4000	0.797	0.504	0.872	0.528
6000	1.179	0.787	1.372	0.828
8000		1.120		1.160

96.4 mole % C₆H₅Cl, log t₀ = 0.788 | 91.5 mole % C₆H₅Cl, log t₀ = 0.745

Pressure	30°	75°	30°	75°
1	0.000	0.190	0.000	0.175
500	0.113	0.078	0.112	0.056
1000	0.223	0.025	0.220	0.054
2000	0.430	0.212	0.427	0.245
4000	0.798	0.515	0.854	0.540
6000	1.123	0.820	1.322	0.839
8000		1.192		1.191

9.9 mole % C₆H₅Cl, log t₀ = 0.433 | 3.5 mole % C₆H₅Cl, log t₀ = 0.423

Pressure	30°	75°	30°	75°
1	0.000	0.143	0.000	0.150
500	0.160	0.006	0.155	0.002
1000	0.310	0.135	0.304	0.130
2000	0.586	0.350	0.581	0.336
4000	1.160	0.658	1.060	0.634
6000	1.552	0.882	1.492	0.878
8000		1.177		1.165

13.0 mole % C₆H₅Cl, log t₀ = 0.435 | 7.6 mole % C₆H₅Cl, log t₀ = 0.424

Pressure	30°	75°	30°	75°
1	0.000	0.120	0.000	0.155
500	0.136	0.004	0.136	0.002
1000	0.270	0.105	0.272	0.125
2000	0.510	0.294	0.505	0.331
4000	0.915	0.605	0.914	0.640
6000	1.298	0.831	1.284	0.851
8000	1.741	1.075	1.640	1.089

9.0 mole % C₆H₅Cl, log t₀ = 0.428 | 95.0 mole % C₆H₅Cl, log t₀ = 0.770

Pressure	30°	75°	30°	75°
1	0.000	0.149	0.000	0.189
500	0.146	0.001	0.115	0.081
1000	0.286	0.127	0.226	0.021
2000	0.547	0.340	0.445	0.209
4000	0.997	0.650	0.855	0.519
6000	1.416	0.872	1.297	0.810
8000	1.880	1.130		1.160

80.0 mole % C₆H₅Cl, log t₀ = 0.700 | 3.0 mole % C₆H₅Cl, log t₀ = 0.425

Pressure	30°	75°	30°	75°
1	0.000	0.190	0.000	0.145
500	0.120	0.075	0.159	0.003
1000	0.240	0.035	0.305	0.125
2000	0.470	0.235	0.566	0.331
4000	0.888	0.563	1.004	0.635
6000	1.319	0.841	1.414	0.887
8000		1.162		1.160

4. n-HEXANE CHLOROBENZENE—*Continued.* (second main column)

11.5 mole % C₆H₅Cl, log t₀ = 0.440

Pressure (kg/cm²)	30°	75°
1	0.000	0.130
500	0.146	0.003
1000	0.284	0.124
2000	0.540	0.330
4000	0.981	0.630
6000	1.391	0.865
8000		1.115

5. n-PENTANE BENZENE

43.8 mole % C₅H₁₂, log t₀ = 0.530 | 11.5 mole % C₅H₁₂, log t₀ = 0.676

Pressure	30°	75°	30°	75°
1	0.000	0.130	0.000	0.153
500	0.115	0.010	0.139	0.037
1000	0.236	0.097	0.271	0.074
1500	0.363	0.195	0.399	0.181
2000	0.494	0.282	0.519	0.282
3000		0.446		0.471
4000		0.590		0.645

66.2 mole % C₅H₁₂, log t₀ = 0.444 | 82.4 mole % C₅H₁₂, log t₀ = 0.375

Pressure	30°	75°	30°	75°
1	0.000	0.120	0.000	0.132
500	0.125	0.002	0.138	0.002
1000	0.243	0.108	0.257	0.115
1500	0.355	0.206	0.362	0.214
2000	0.460	0.292	0.455	0.302
3000	0.656	0.446	0.614	0.454
4000		0.576		0.581

28.0 mole % C₅H₁₂, log t₀ = 0.600 | 52.3 mole % C₅H₁₂, log t₀ = 0.500

Pressure	30°	75°	30°	75°
1	0.000	0.131	0.000	0.119
500	0.130	0.054	0.120	0.003
1000	0.260	0.080	0.236	0.116
1500	0.384	0.179	0.347	0.220
2000	0.503	0.274	0.449	0.314
3000		0.445		0.479
4000				0.625

75.1 mole % C₅H₁₂, log t₀ = 0.405 | 59.2 mole % C₅H₁₂, log t₀ = 0.475

Pressure	30°	75°	30°	75°
1	0.000	0.130	0.000	0.115
500	0.134	0.003	0.128	0.004
1000	0.254	0.110	0.247	0.100
1500	0.359	0.212	0.359	0.195
2000	0.453	0.302	0.454	0.284
3000		0.455	0.626	0.440
4000		0.590		0.580

36.2 mole % C₅H₁₂, log t₀ = 0.565 | 19.8 mole % C₅H₁₂, log t₀ = 0.642

Pressure	30°	75°	30°	75°
1	0.000	0.136	0.000	0.175
500	0.133	0.004	0.127	0.051
1000	0.254	0.119	0.250	0.064
1500	0.362	0.227	0.367	0.169
2000	0.470	0.325	0.480	0.267
3000	0.668	0.500	0.689	0.442
4000		0.704		

92.5 mole % C₅H₁₂, log t₀ = 0.339 | 5.0 mole % C₅H₁₂, log t₀ = 0.710

Pressure	30°	75°	30°	75°
1	0.000	0.150	0.000	0.181
500	0.157	0.016	0.148	0.046
1000	0.296	0.146	0.290	0.078
1500	0.423	0.249	0.424	0.188
2000	0.537	0.332	0.550	0.290
3000	0.755	0.467		0.463
4000		0.567		

74.5 mole % C₅H₁₂, log t₀ = 0.407

Pressure	30°	75°
1	0.000	0.120
500	0.126	0.001
1000	0.251	0.110
1500	0.369	0.209
2000	0.476	0.290
3000	0.671	0.301

6. EUGENOL CARBON DISULPHIDE[6]

28.2 mole % C₁₀H₁₂O₂, log t₀ = 0.418 | 76.0 mole % C₁₀H₁₂O₂, log t₀ = 0.429

Pressure (kg/cm²)	30°	75°	30°	75°
1	0.000	0.188	0.000	0.400
500	0.115	0.096	0.179	0.281
1000	0.223	0.007	0.357	0.159
2000	0.429	0.169	0.740	0.090
4000	0.819	0.490	1.572	0.611
6000	1.195	0.769	2.470	1.176
8000		1.011		1.828

10.1 mole % C₁₀H₁₂O₂, log t₀ = 0.650 | 20.7 mole % C₁₀H₁₂O₂, log t₀ = 0.770

Pressure	30°	75°	30°	75°
1	0.000	0.128	0.000	0.170
500	0.079	0.048	0.095	0.066
1000	0.157	0.026	0.184	0.030
2000	0.307	0.161	0.359	0.200
4000	0.581	0.385	0.720	0.461
6000	0.817	0.583	1.112	0.653
8000		0.752		0.799

48.5 mole % C₁₀H₁₂O₂, log t₀ = 0.715 | 39.6 mole % C₁₀H₁₂O₂, log t₀ = 0.382

Pressure	30°	75°	30°	75°
1	0.000	0.300	0.000	0.190
500	0.149	0.175	0.109	0.121
1000	0.293	0.053	0.216	0.051
2000	0.597	0.120	0.442	0.100
4000	1.213	0.579	0.996	0.420
6000	1.975	1.011	1.419	0.782
8000		1.480		1.210

94.0 mole % C₁₀H₁₂O₂, log t₀ = 0.653 | 5.1 mole % C₁₀H₁₂O₂, log t₀ = 0.155

Pressure	30°	75°	30°	75°
1	0.000	0.438	0.000	0.080
500	0.238	0.293	0.074	0.038
1000	0.470	0.148	0.143	0.034
2000	0.934	0.148	0.273	0.150
4000	2.052	0.765	0.490	0.354
6000		1.439	0.694	0.530
8000				0.680

61.2 mole % C₁₀H₁₂O₂, log t₀ = 0.793 | 43.8 mole % C₁₀H₁₂O₂, log t₀ = 0.446

Pressure	30°	75°	30°	75°
1	0.000	0.325	0.000	0.131
500	0.169	0.184	0.133	0.010
1000	0.340	0.048	0.264	0.104
2000	0.677	0.192	0.527	0.319
4000	1.334	0.642	1.090	0.697
6000	2.186	1.046	1.728	1.042
8000		1.541		1.490

6.1 mole % C₁₀H₁₂O₂, log t₀ = 0.627 | 35.3 mole % C₁₀H₁₂O₂, log t₀ = 0.370

Pressure	30°	75°	30°	75°
1	0.000	0.095	0.000	0.190
500	0.075	0.022	0.102	0.011
1000	0.146	0.048	0.206	0.025
2000	0.282	0.178	0.420	0.150
4000	0.527	0.401	0.889	0.510
6000	0.754	0.580	1.395	0.880
8000		0.731		1.278

2.4 mole % C₁₀H₁₂O₂, log t₀ = 0.563 | 84.7 mole % C₁₀H₁₂O₂, log t₀ = 0.370

Pressure	30°	75°	30°	75°
1	0.000	0.105	0.000	0.410
500	0.072	0.031	0.195	0.285
1000	0.141	0.036	0.394	0.159
2000	0.271	0.160	0.813	0.110
4000	0.495	0.358	1.760	0.669
6000	0.683	0.509	2.800	1.283
8000		0.622		2.018

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[6]The viscosities at atmospheric pressure t₀ cannot be compared for those mixtures for which different falling-weights were used for different concentrations. This was the case for the eugenol carbon disulphide mixtures; two viscometers with different falling-weights were used.

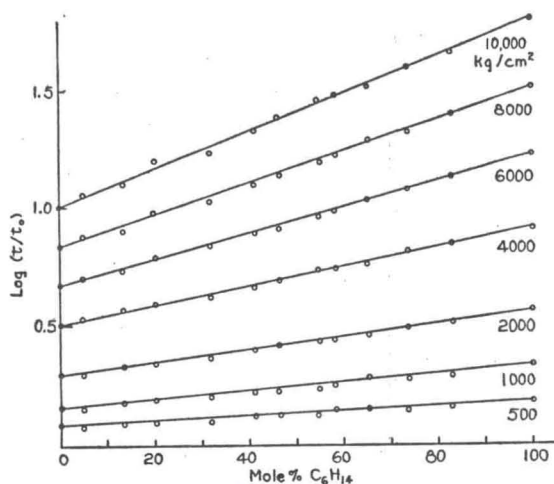FIG. 1. Relative viscosity at 30° of n-hexane carbon disulphide against concentration.

FIG. 2. Relative viscosity at 30° of n-hexane n-decane against concentration.

slipping over each other. Raman and Krishnan[7] from their studies on birefringence have considered that there is a tendency for nonspherical molecules to orientate under mechanical stress within a liquid; moreover, such an arrangement is most probable for a statistical energy distribution.

Increase of pressure at constant temperature could not be expected to cause any irregularity in the orientation; rather, it should increase the uniformity of it. Bridgman's[8] comment on this point is applicable to the present results: "Along with the idea of molecules with shape goes the conception that at high pressures these shapes must be forced more or less to adapt themselves to each other; in other words, the molecules must begin to show traces of regular arrangement. The regularity is by no means the thorough-going regularity of a crystal in which the molecules are permanently moored to certain mean positions, the molecules of the liquid still circulate about among each other, but as they slide past each other there may be a growing tendency at higher pressures to point the long axes in the direction of relative motion, for example. This increasing order of arrangement seems not only natural, but inevitable at high pressures." Increase of temperature would tend to break up the parallel orientation by increasing the thermal agitation.

Under these conditions, the interlocking of molecules probably takes place in a simple way.

There have been several equations proposed for the viscosity of binary mixtures of chemically indifferent liquids

$$\eta = \eta_1{}^x \eta_2{}^{(1-x)}, \text{ Arrhenius.[9]} \tag{1}$$

$$\eta = \eta_1 x + \eta_2(1-x), \text{ Kendall and Monroe.[10]} \tag{2}$$

$$\varphi = \varphi_1 x + \varphi_2(1-x), \text{ Bingham.[11]} \tag{3}$$

$$\eta = \eta_1 + (\eta_2 - \eta_1) K_2 a_2 Z_m / K_1 a_1 (1 - Z_m)$$
$$+ K_2 a_2 Z_m, \text{ Ishikawa.[12]} \tag{4}$$

$$\varphi = \varphi_1 a + \varphi_2 b - K(a-m)(v_1 - v_2),$$
$$\text{Bingham and Brown.[13]} \tag{5}$$

$$\log \eta = m \cdot \log \eta_1 + (1-m) \log \eta_2$$
$$- \int (q_m / R \cdot T^2) dT, \text{ Lederer.[14]} \tag{6}$$

$$L_m = x L_a + (1-x) L_b$$
$$L_m' = x L_1' + (1-x) L_2' + Cx(1-x),$$
$$\text{Cragoe.[15]} \tag{7}$$

In these formulae, η is the viscosity of the mixture, φ the fluidity, $\eta_1, \eta_2, \varphi_1, \varphi_2$, the viscosities and fluidities, respectively, of the components. It has been usual to consider x as the volume,

[7] C. V. Raman and K. S. Krishnan, Phil. Mag. 5, 767 (1928).
[8] P. W. Bridgman, Proc. Am. Acad. 42, 111 (1913).

[9] S. Arrhenius, Zeits. f. physik. Chemie 1, 285 (1887).
[10] J. Kendall and K. P. Monroe, J. Am. Chem. Soc. 39, 1802 (1917).
[11] E. C. Bingham, J. Am. Chem. Soc. 35, 195 (1906).
[12] T. Ishikawa, Bull. Chem. Soc. Jap. 4, 5 (1929).
[13] E. C. Bingham and D. F. Brown, J. Rheology 3, 95 (1932).
[14] E. L. Lederer, Kolloid-Bei. 34–35, 270 (1932).
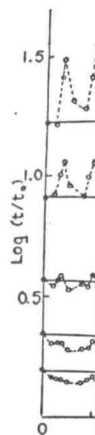[15] C. S. Cragoe, Proc. World Petroleum Congress, London F, 529 (1933).

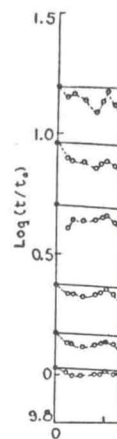FIG. 3. Relative viscosity at 30° of *n*-hexane chlorobenzene against concentration.

FIG. 5. Relative viscosity at 30° of *n*-hexane diethyl ether against concentration.
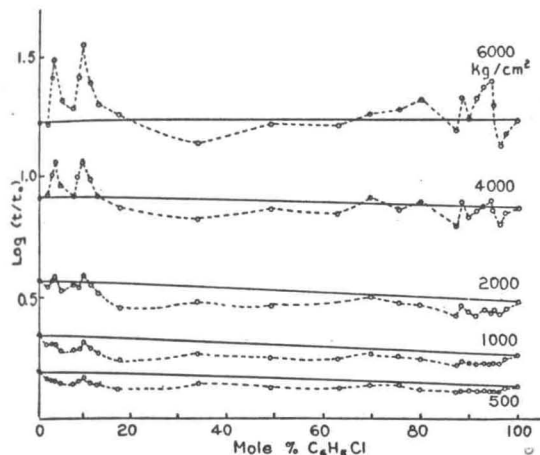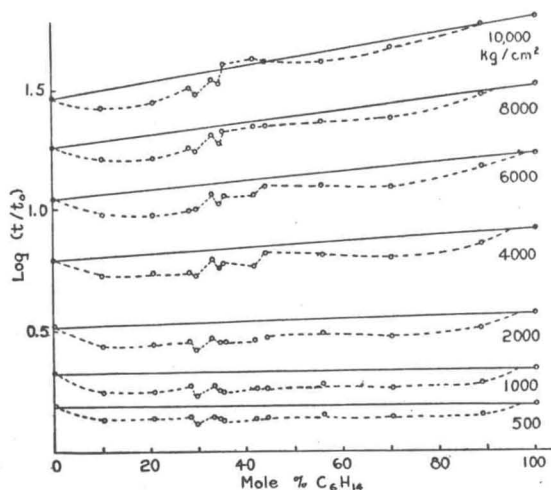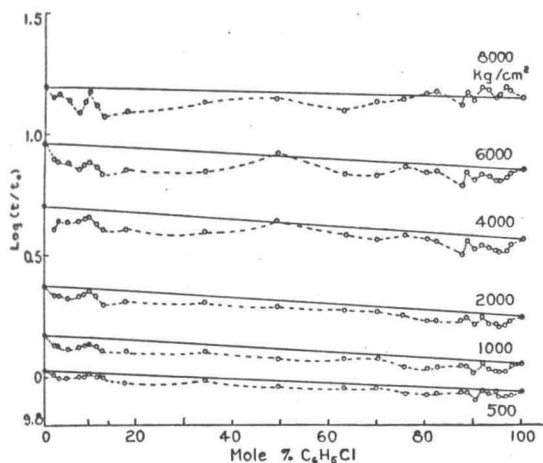

FIG. 4. Relative viscosity at 75° of *n*-hexane chlorobenzene against concentration.
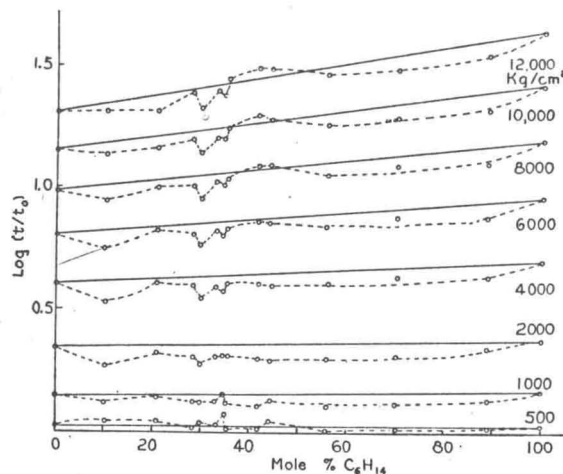

FIG. 6. Relative viscosity at 75° of *n*-hexane diethyl ether against concentration.

weight and molar fractions, indiscriminately. For an explanation of the other symbols used in Eqs. (4) to (7) the reader is referred to the original papers.

The two mixtures of the first group, *n*-hexane carbon disulphide and *n*-hexane *n*-decane, obey Arrhenius' empirical equation of mixture. In these cases, the pressure and temperature coefficients of viscosity of the components are additive in mixture, assuming no relative change in concentration with pressure and temperature change, for since

$$\eta = \eta^x \eta^{(1-x)},$$
$$\log_e \eta = x \log_e \eta_1 + (1-x) \log_e \eta_2,$$

and $1/\eta \, d\eta/dp = x/\eta_1(d\eta_1/dp) + 1 - x/\eta_2(d\eta_2/dp)$;
also, $1/t \, d\eta/dt = x/\eta_1(d\eta_1/dt) + 1 - x/\eta_2(d\eta_2/dt)$.

Consequently, it seems probable that the simple picture of interlocking of the long, similarly oriented molecules in these mixtures has some validity for one would not expect this type of interlocking to vary much with the concentration.

The log viscosity curves[16] of *n*-hexane diethyl

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[16] Dotted lines have been drawn through the computed points while the solid straight lines in the figures represent the behavior of a mixture in which the pressure and temperature coefficients of viscosity of the components are additive. It is convenient to use these lines as bases of reference for the discussion of the actual curves.
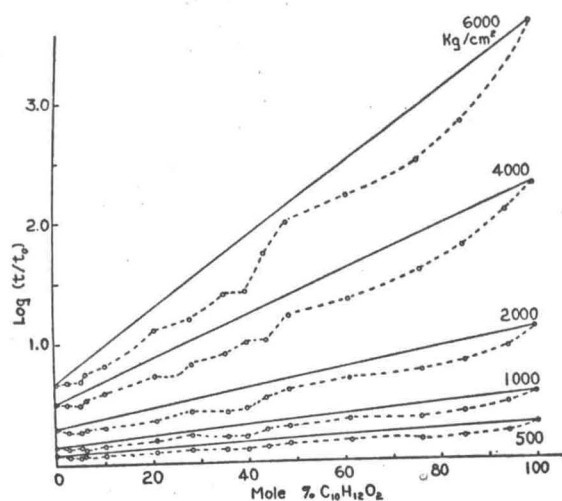
FIG. 7. Relative viscosity at 30° of eugenol carbon disulphide against concentration.
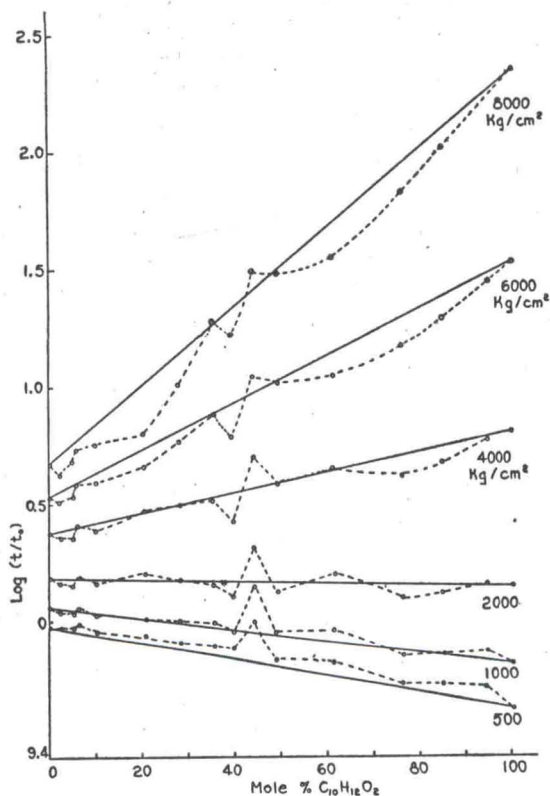

FIG. 8. Relative viscosity at 75° of eugenol carbon disulphide against concentration.

ether, *n*-hexane chlorobenzene, *n*-pentane benzene, and eugenol carbon disulphide display various kinds of irregularities which are in no way similar for these mixtures. For example, the
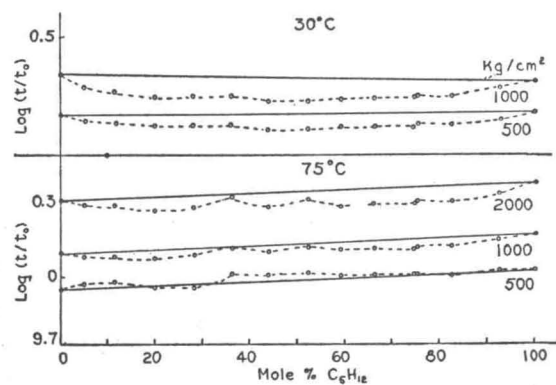

FIG. 9. Relative viscosity at 30° and 75° of *n*-pentane benzene against concentration.

peaks in the hexane chlorobenzene isobars do not appear on the corresponding pentane benzene curves; also, the same curves for hexane ether exhibit distinctive complexities. Inasmuch as these mixtures of the second group, with the exception of pentane benzene, contain a polar component, it is possible that complexes or associations of molecules will affect the results. Although the effects of association, as judged by the departures of the density-concentration curves from linearity do not seem to be significant for the viscosity of the mixtures at atmospheric pressure, the effects at high pressures may play important parts in the observed viscosity. While the final free space arrangement of the molecules depends little on whether the molecules are in a combined or free state, it is clear that the effect on viscosity will be different, for the mechanism of viscous resistance involves relative motion of interlocked structures which in turn will depend on the molecules of the mixtures.

Bridgman[17] in discussing association as applied to his results on water at high pressures prefers to leave open the question of whether pressure increases or decreases the amount of association, although his results suggested that pressure merely influenced the effects of association without necessarily changing the amount. Collins,[18] from an investigation of the infrared absorption spectra of liquids known to associate, concludes that his results indicated no change in association

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[17] P. W. Bridgman, Proc. Am. Acad. 47, 546 (1912).
[18] J. R. Collins, Phys. Rev. 39, 305 (1930).

with change of pressure. Whether or not the degree of association changes with pressure, the effect of association apparently changes with pressure, becoming stronger with increase of pressure and consequently complicating the interlocking.

From these considerations it appears probable that the interlockings in this group of mixtures are complicated by the structural differences of the component molecules and their effects. Thus the observed complexities in the viscosity isobars, Figs. 3 to 9 inclusive, are unique functions of mixture and they display such bewildering variations with concentration that it seems hopeless to attempt to express the viscosity at high pressures by a quantitative relation. It may be stated that the irregularities observed in the viscosity are of such magnitudes that it is impossible to consider them as due to experimental errors.

The results for the n-pentane benzene mixtures are significant. While these mixtures might be classed with those in the first group, since all are composed of nonpolar components, it is evident, however, from an inspection of Fig. 9 that the interlocking must be quite different. The departures of the viscosity isobars from linearity at 30° are in the nature of sags which extend uniformly over the concentration range and which vary greatly with pressure. But at 75°, the sags are much different, being absent or less in amount at the corresponding pressures; however, at the highest pressure, the qualitative natures of the curves become more nearly similar to those at 30°. There is no reason for abnormality in the pentane benzene mixtures due to such effects as previously discussed and the interlocking would be thought characteristic of the component molecules.

A complete explanation of the sags in the viscosity isobars of the n-pentane benzene mixtures would necessitate more exact information about viscous interlocking. Yet, it does not seem unlikely that a change in orientation with change of pressure, effected in such a way that there is a tendency for the flat planes of the benzene molecules to become parallel with the direction of relative motion, might conceivably result in an interlocking not unlike that which has been considered in the first group of mixtures. This particular type of interlocking in pentane benzene mixtures offers a qualitative explanation of a relative viscosity less than that obtained if the pressure and temperature coefficients of viscosity of the components were additive in mixture.

CONCLUSIONS

The log viscosity for two mixtures, n-hexane carbon disulphide and n-hexane n-decane at different pressures and temperatures, has been shown to obey Arrhenius' equation for the viscosity of a binary mixture, indicating that the pressure and temperature coefficients of viscosity of the components are additive. It is believed that a comparatively simple type of interlocking occurs in these mixtures due to the effectively linear structure of the molecules and the absence of non-uniform molecular fields such as would cause some sort of association. For the mixtures n-hexane diethyl ether, n-hexane chlorobenzene, n-pentane benzene, and eugenol carbon disulphide, few generalities can be stated about association of molecules and the resulting kinds of interlocking at high pressures for they are specific properties of mixture.

The viscosity of liquids is not at all well understood notwithstanding the theoretical advances of Raman[19] and Andrade.[20] While the viscosity of liquids at high pressures represents somewhat unusual experimental conditions, nevertheless it displays those salient features of structure which exist in liquids at more normal conditions but which probably are less effective in the comparatively large "free-space." Considering the results of this investigation, viscosity is a specific property of the molecule and as such it offers prohibitive difficulties for any complete, theoretical generalizations at present.

This problem was suggested to the author by Professor P. W. Bridgman and it is a pleasure to acknowledge his interest and cooperation.

[19] C. V. Raman, Nature 3, 532 (1923); 3, 600 (1923).
[20] E. N. da C. Andrade, Phil. Mag. 17, 497 (1934), and 17, 698 (1934).

Errata: The Flow Characteristics of Sewage Sludge and Other Thick Materials

WILHELM MERKEL, *Stuttgart*
(Physics 5, 355, 1934)

IN Fig. 2 of this paper there are some changes. The correct figure is published here.
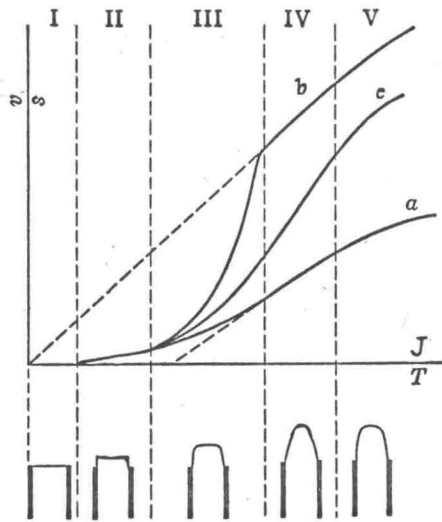

FIG. 2. The five types of flow of plastic bodies. Velocity distribution over bore of tubes. v and J are velocity and gradient in the tube. s and T are the shear and torque in the rotation viscometer. The lower part of figure shows variation in velocity across the pipe section.