Viscosities of Some Organic Glasses Used as Trapping Matrices. III

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The temperature dependence of viscosity for glycerol, glycerol triacetate, propylene glycol, 1:1 v/v mixture of ethanol and methanol, 1:1 and 3:2 v/v mixtures of *n*-propanol and isopropanol, 1:1 v/v and 2:3 v/v mixtures of methylcyclopentane and methylcyclohexane, and 1:1 v/v mixture of 2-methylpentane and methylcyclohexane has been determined between the limits of 10^5 to 10^{12} P. Measurements on *n*-propanol have been extended to 3×10^{11} P. Viscosity measurements at temperatures beyond the glass-transition region and greater than 10^{13} P were attempted unsuccessfully.

Diffusion processes, trapping and decay of radiation produced species, luminescence lifetimes, and kinetic rate phenomena in general, all seem to exhibit a partial dependence on rheological parameters. To study such kinetic processes more fully, we have extended earlier studies (*3*, *4*) to include new compounds and mixtures of compounds.

EXPERIMENTAL

Viscosities were determined using gravity-fall (*15*), or pressure-extrusion (*15*), methods. Temperature control was achieved by a gaseous nitrogen flow system, and temperature measurement via a copper-constantan thermocouple reading through a microvoltmeter and chart recorder. Experimental methods were similar to those described previously (*3*, *4*) but utilizing modified viscometer tubes (Figure 1) to extend the useful range of viscosity measurement. Aluminum foil was the most satisfactory material to close these viscometers prior to the introduction of the sample, glycerol being used to seal the edges as in previous work. On occasion, use was made of commercially supplied polymer films such as Stretch 'n Seal (Colgate-Palmolive Co.) or Handi-Wrap (Dow Chemical Co.) instead of the aluminum foil, but neither metal nor glass plates proved satisfactory for sealing the viscometer.

Glass viscometer tubes of 5.55 and 9.50-cm diameters were used with helium pressures up to 100 psi. To investigate high-viscosity materials, a stainless-steel viscometer was constructed (Figure 1a). To help secure the plug against slippage and helium leaks, a $^3/_{16}$-in. lip was machined into the lower surface of the tube. This reduced the effective diameter of the tube to 14.30 cm. Viscosities were calculated from $\eta = PR^2t/4\ HL$ (pressure extrusion method), where R is the tube radius, H the height of the plug, and L the extrusion produced by pressure P for time t; or from $\eta = \rho g R^2 t/4\ L$ (gravity-fall method) where ρ is the density of the plug, g the acceleration due to gravity, and R, L, and t, as before. Use of cgs units lead to viscosity coefficients η in units of poises.

Values for the density ρ were obtained either from the literature, or by use of room temperature values and approximate contraction data obtained experimentally, or by assuming an arbitrary value by analogy with other available data. Specific gravity values and respective temperature ranges used to calculate viscosity coefficients were: glycerol 1.32 between 210–20K (*7*), glycerol triacetate (triacetin) 1.28 between 215–25K (*5*), propylene glycol 1.20 between 180–90K (*8*, *11*, *12*), methanol/ethanol mixtures 0.93 between 110–20K (*11*, *12*), *n*-propanol/isopropanol mixtures 0.98 between 120–30K (*11*, *12*), methyl-*cyclo*-pentane/methyl-*cyclo*-hexane mixtures 1.00 between 95–100K (*3*, *4*, *11*, *12*). Viscosity data at the higher temperatures obtained by gravity-fall methods are therefore subject to the inherent error caused by limitations in known density data.

All materials were used directly as supplied, and mixtures were made on a volume-volume basis. Anhydrous methanol (MeOH) and anhydrous ethanol (EtOH) were supplied by Merck Chemical Co.; *n*-propanol (nP) and isopropanol (iP)

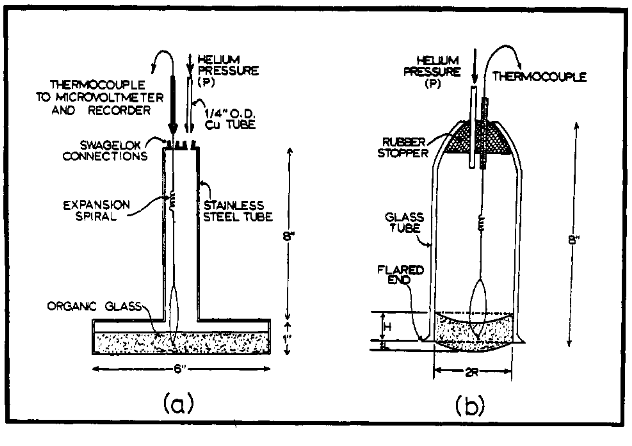

Figure 1. Viscometer tubes

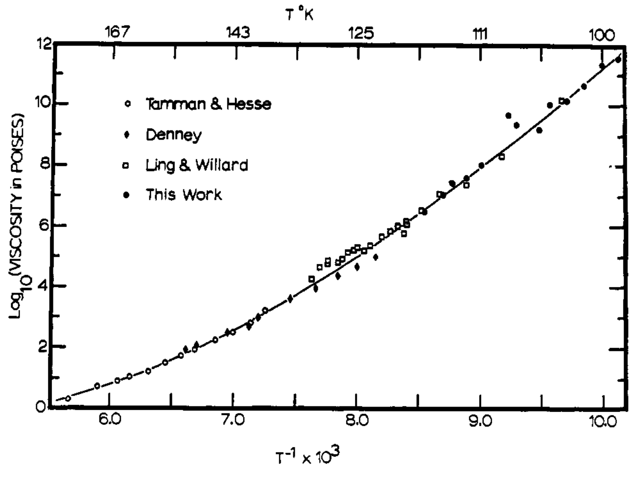

Figure 2. Temperature dependence of viscosity for *n*-propanol

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Table I. Temperature Dependence of Viscosity for Some Organic Glasses

T, K	Viscosity, P
A. MCP/MCH (1:1)	
82.0	4.57×10^{9}
83.0	7.27×10^{8}
83.5	6.38×10^{8}
84.0	2.21×10^{8}
87.5	1.34×10^{6}
88.0	1.29×10^{6}
B. MCP/MCH (2:3)	
85.5	3.03×10^{9}
92.5	2.15×10^{6}
94.0	7.52×10^{5}
95.0	7.09×10^{5}
95.5	3.99×10^{5}
96.0	3.97×10^{5}
97.0	1.62×10^{5}
C. MCH/2MP (1:1)	
95.0	1.68×10^{7}
96.5	1.20×10^{7}
97.5	4.33×10^{6}
99.0	9.50×10^{5}
99.0	1.42×10^{6}
100.0	7.07×10^{5}
D. MeOH/EtOH (1:1)	
97.5	7.71×10^{11}
98.5	1.15×10^{11}
100.5	1.69×10^{10}
102.5	5.87×10^{9}
104.5	5.82×10^{8}
105.5	2.66×10^{8}
106.5	1.24×10^{8}
107.5	6.17×10^{7}
108.5	3.66×10^{7}
109.5	8.22×10^{6}
111.0	2.69×10^{6}
112.0	2.34×10^{6}
113.0	3.73×10^{5}
115.0	1.17×10^{5}
116.0	4.50×10^{4}
117.5	1.04×10^{4}
E. PG	
167.5	6.97×10^{9}
169.0	1.32×10^{10}
172.0	2.54×10^{9}
172.0	8.68×10^{8}
173.0	5.37×10^{8}
173.0	4.72×10^{8}
174.5	4.42×10^{8}
180.0	5.81×10^{7}
182.0	1.45×10^{7}
186.0	1.48×10^{7}
187.5	9.95×10^{6}
189.0	6.32×10^{6}
189.5	5.39×10^{6}
190.0	5.49×10^{6}
F. Triacetin[a]	
206.0	6.49×10^{8}
213.0	9.40×10^{7}
213.5	5.87×10^{7}
214.0	7.31×10^{7}
214.0	6.07×10^{7}
214.0	2.95×10^{7}
215.5	2.75×10^{7}
217.0	4.42×10^{6}
217.5	6.36×10^{6}
217.5	1.58×10^{6}
218.5	2.01×10^{6}
218.5	7.89×10^{6}
219.0	1.08×10^{7}
219.5	1.06×10^{6}
219.5	2.29×10^{7}
220.0	4.97×10^{7}
220.5	1.54×10^{7}
221.5	6.98×10^{6}
222.5	9.41×10^{6}
223.5	1.88×10^{6}
223.5	2.39×10^{5}
224.0	1.52×10^{6}
225.0	8.83×10^{5}
225.0	3.85×10^{5}
225.5	4.03×10^{5}
G. Glycerol[a]	
192.5	6.08×10^{10}
193.5	2.90×10^{10}
194.5	2.51×10^{10}
196.5	6.27×10^{9}
197.0	4.45×10^{9}
197.5	5.05×10^{9}
198.0	3.09×10^{9}
199.0	3.14×10^{9}
200.0	3.22×10^{9}
202.0	1.13×10^{9}
202.5	8.01×10^{8}
204.5	4.19×10^{8}
205.5	2.06×10^{8}
207.0	1.05×10^{8}
209.0	2.75×10^{7}
211.5	5.08×10^{7}
212.5	3.34×10^{7}
213.5	2.14×10^{7}
214.0	2.66×10^{7}
214.5	2.26×10^{7}
215.0	1.80×10^{7}
215.5	1.47×10^{7}
216.5	1.06×10^{7}
217.5	1.10×10^{7}
217.5	9.76×10^{6}
218.5	9.83×10^{6}
H. *n*-Propanol	
98.5	3.17×10^{11}
100.0	2.11×10^{11}
101.5	4.51×10^{10}
103.0	1.33×10^{10}
104.5	1.11×10^{10}
105.5	1.45×10^{9}
108.0	2.27×10^{9}
108.5	4.75×10^{9}
111.0	1.02×10^{8}
112.5	3.95×10^{7}
114.0	2.41×10^{7}
115.0	1.05×10^{7}
117.0	2.97×10^{6}
I. nP/iP (1:1)	
107.5	4.35×10^{10}
110.0	3.33×10^{9}
110.5	5.37×10^{8}
111.0	1.02×10^{9}
111.0	1.64×10^{9}
112.0	1.05×10^{9}
113.5	1.30×10^{8}
114.0	6.59×10^{8}
114.5	1.58×10^{8}
115.0	2.71×10^{8}
115.5	2.93×10^{7}
117.0	3.00×10^{7}
118.5	1.64×10^{7}
119.5	7.37×10^{6}
120.0	9.90×10^{6}
121.0	2.02×10^{7}
121.5	6.04×10^{6}
123.0	2.30×10^{6}
123.5	1.81×10^{6}
124.0	2.89×10^{6}
124.5	9.35×10^{5}
127.5	2.80×10^{5}
128.5	2.04×10^{5}
J. nP/iP (3:2)	
104.5	5.57×10^{10}
106.5	1.24×10^{10}
107.0	7.74×10^{9}
111.5	1.27×10^{8}
112.0	2.36×10^{8}
112.5	1.81×10^{8}
114.0	6.73×10^{7}
116.0	1.72×10^{7}
118.5	1.57×10^{7}
118.5	8.80×10^{6}
119.0	9.54×10^{6}
119.5	6.74×10^{6}
120.0	5.25×10^{6}
120.5	9.76×10^{6}
120.5	3.15×10^{6}
121.0	3.21×10^{6}
121.5	2.52×10^{6}
121.5	5.25×10^{6}
122.0	2.48×10^{6}
123.0	2.08×10^{6}
123.5	1.35×10^{6}
123.5	7.15×10^{5}

[a] Solid CO_2 (T = 194.5K) used as reference junction for thermocouple.

were Fischer Certified Grade; glycerol, glycerol triacetate (triacetin), propylene glycol (PG), 2-methylpentane (2MP), methyl-*cyclo*-hexane (MCH), and methyl-*cyclo*-pentane (MCP), were supplied by Aldrich Chemical Co.

RESULTS

To evaluate the viscometer tubes used in this work, the viscosity-temperature dependence of *n*-propanol was studied, extending data to beyond 10^{11} P and obtaining satisfactory agreement with previous results (*3*, *4*) (Table I and Figure 2). That mutually consistent viscosity values are obtained from these viscometers is further supported by the data for glycerol and triacetin, shown in Figure 3, where a smooth curve is obtained extending from room-temperature viscosities ca. 10^{-2} P to low-temperature viscosities ca. 10^{10} P.

Although neither anhydrous methanol nor anhydrous ethanol will form a glass, a 1:1 mixture of these pure components will do so; data for such a mixture are given in Table I. Viscosity-temperature data for propylene glycol, glycerol, *n*-propanol, *n*-propanol/isopropanol mixtures (1:1 and 3:2 v/v), methyl-*cyclo*-pentane and methyl-*cyclo*-hexane mixtures (1:1 and 2:3 v/v), and a 1:1 v/v mixture of 2-methylpentane and methyl-*cyclo*-hexane, are given in Table I and displayed graphically in Figure 4.

Data have been correlated by the straight-line relationship of Equation 1:

$$\log \eta = AT^{-1} + B \qquad (1)$$

and the parameters to this equation determined by a least-squares fit to the data (Table II). Activation energies for viscous flow (E) calculated from Equation 2

$$\eta = \eta_0 \exp(-E/kT) \qquad (2)$$

are given in Table II, together with the straight-line extrapolation value for the viscosity coefficient at 77.5K (see Discussion below).

Table II. Viscosity Data for Some Organic Glasses

	$A \times 10^{-3}$, K^{-1}	$-B$	$-E$ eV	$-E$ Kcal/mol	Correl. coeff.	Viscosity at 77.5K, extrap., P
Triacetin	7.258	26.32	1.440	33.2	0.8364	2.40×10^{67}
Glycerol	6.080	21.07	1.207	27.8	0.9887	2.64×10^{57}
PG	4.522	17.22	0.898	20.7	0.9731	1.45×10^{41}
nP[a]	2.919	18.15	0.579	13.4	0.9908	3.42×10^{19}
nP/iP (1:1)[b]	3.148	18.21	0.625	14.4	0.9763	2.64×10^{21}
nP/iP (3:2)[b]	2.983	18.13	0.592	13.7	0.9858	2.44×10^{20}
MCP/MCH (1:1)[b]	4.387	43.86	0.871	20.1	0.9976	5.88×10^{12}
MCl/MCH (2:3)[b]	3.067	26.53	0.609	14.0	0.9912	1.18×10^{13}
MeOH/EtOH (1:1)[b]	4.275	32.09	0.848	19.6	0.9980	1.26×10^{23}
2 MP/MCH (1:1)[b]	2.988	23.28	0.577	13.3	0.9788	1.98×10^{14}

[a] Values for A and B obtained by using data from this work and previous work (*3*, *4*). [b] Mixtures formed on a volume/volume basis.

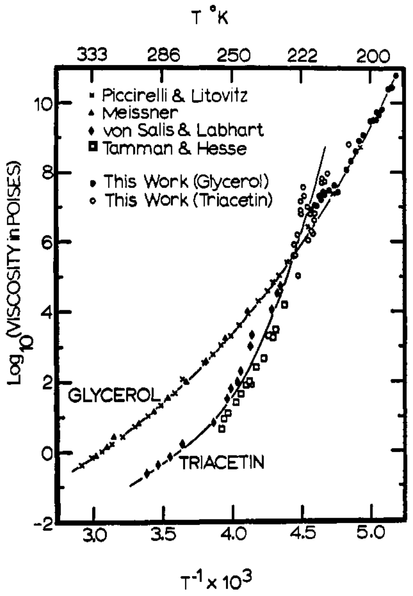

Figure 3. Temperature dependence of viscosity for glycerol and triacetin

Piccirelli and Litovitz (*9*), Meissner (*6*), Von Salis and Labhart (*14*), Tamman and Hesse (*13*)

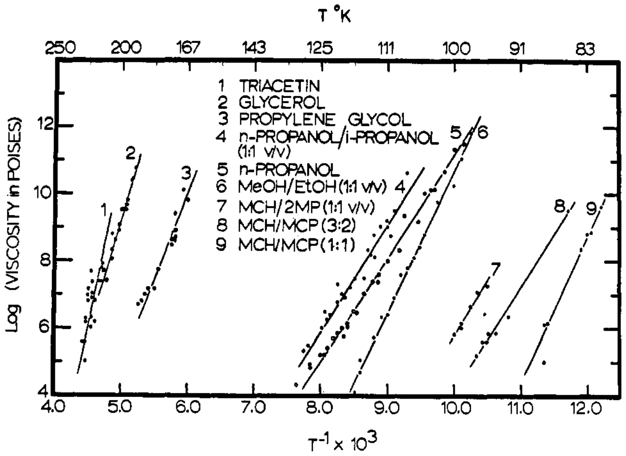

Figure 4. Temperature dependence of viscosity for some organic glasses

DISCUSSION

In previous work (*3*, *4*), it was noted that a linear extrapolation of the data to furnish a value for the viscosity at the temperature of boiling liquid nitrogen was probably most inaccurate. Apart from the inherent error produced by a long extrapolative procedure, the more significant factor is that the data obtained do not traverse the glass-transition region (gtr). If viscosity measurements were made with the temperature *decreasing* smoothly and progressively on a plug formed at temperatures higher than those in the gtr (or one that has been allowed to equilibrate for a long period at a temperature higher than those in the gtr), then a series of data pairs lying on a smooth curve (correlated by a straight-line logarithmic relationship above) is obtained.

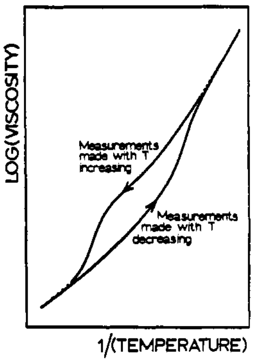

Figure 5. Apparent "hysteresis" behavior on measurement of temperature dependence of viscosity for organic glasses in vicinity of glass transition region

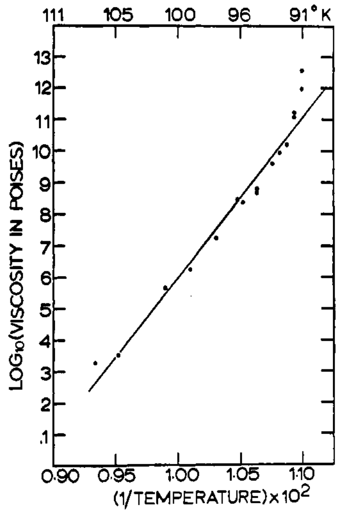

Figure 6. Temperature dependence of viscosity for methyltetrahydrofuran glass between 91 and 108K

However, if data are taken by *increasing* the temperature

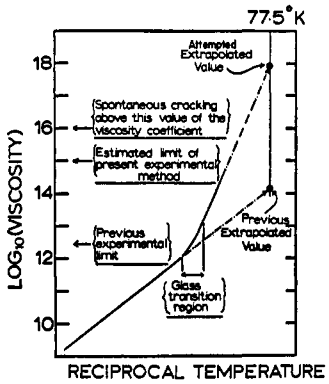

Figure 7. *Postulated* behavior of viscosity coefficient as function of temperature, and details of attempted extrapolation procedure to obtain more meaningful viscosity data for organic glasses at 77K

from some arbitrary initial value close to the gtr (i.e., viscosity coefficients at about 10^{12} to 10^{13} P), using a plug formed by freezing to a temperature below the gtr, a curve with several anomalously high points in the low-temperature region is obtained. This "hysteresis" behavior is shown diagrammatically in Figure 5, and is demonstrated by the viscosity-temperature dependence of 2-methyltetrahydrofuran shown in Figure 6, where data from ref. *3* and experimental data at 91K illustrate the anomalously high values at low temperatures relative to the high-temperature region. These high values may be accounted for by assuming that insufficient time was allowed for molecular relaxation to occur at temperatures close to the gtr, where molecular relaxation time scales are becoming comparable with experimental time scales (use of longer equilibration times prior to measurement will move the apparent glass-transition region to lower temperatures).

It seems probable, therefore, that a discontinuity in the viscosity-temperature dependence might be noted in the region of the glass transition, and that any extrapolation through this region will be subject to an error caused by the postulated discontinuity. To obtain a better estimate of viscosity coefficients at 77.5K, the commonly used temperature for matrix isolation studies in several disciplines, measurements of viscosities at values beyond 10^{12} P were attempted in order to span the gtr and obtain a more valid extrapolation (see the diagrammatic representation in Figure 7). For this purpose, the metal viscometer (Figure 1a) was constructed utilizing as large a diameter tube as could be accommodated in the gas-flow cryostat. Provided a satisfactory organic-glass plug could be formed, it was estimated that the experimental viscosity limit would be of the order 10^{15} P.

Unfortunately, at no time was a suitable plug formed in the viscometer. Two major reasons appeared to contribute to this lack of success. It has already been pointed out (*3*) that in a small viscometer tube (<1-in. diam) "spontaneous" cracking of the glass plug occurs when the temperature is such as to correspond to a viscosity of ca. 10^{16} P. For larger diameter plugs (ca. 5 in.) it seems sufficient for the viscosity to approach 10^{13}–10^{14} P for this to happen. The large-diameter plug also makes it virtually impossible to anneal out the cracks by gentle warming and re-cooling, due to the severe deformation (gravity fall) at relatively high viscosities (10^{10} P). The second shortcoming involved poor sealing between the metal viscometer and organic glass, leading to persistent helium leakage and therefore pressure and temperature fluctuations.

Attempts to measure viscosity coefficients in the glass-transition region have thus far been unsuccessful by this method. The only comparable measurements to these are those by Davies and Jones (*1*) on glucose, and by Plazek and Magill on 1,3,5-tri-α-naphthyl benzene (*10*). Neither investigation shows a discontinuity at the 10^{12}–10^{13}-P region. However, Davies and Jones emphasize that their glucose specimens were allowed ample time to stabilize with respect to temperature equilibration which would obviate the "hysteresis" effects noted here.

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RECEIVED for review November 1, 1971. Accepted January 7, 1972. The Research Corporation partially supported this project, and one of us (R. J. C.) received from the National Science Foundation an Undergraduate Summer Research Participation Scholarship. Presented in part at the South-East/South-West Joint Regional Meeting of the American Chemical Society, December 1970, New Orleans, LA. For Parts I and II of this series see refs *3* and *4*, respectively.