Viscosities of Some Organic Glasses Used as Trapping Matrices[1]

by A. Campbell Ling and John E. Willard

Department of Chemistry, University of Wisconsin, Madison, Wisconsin (Received January 2, 1968)

The viscosities of eight organic glasses have been determined as a function of temperature over the viscosity range of approximately 10^4 to 10^{12} P. The compounds and absolute temperatures investigated are: 3-methylpentane, 94–77°; 2-methylpentane, 96–80°; 2-methylpentene-1, 102–88°; 2-methyltetrahydrofuran, 107–92°; n-propyl alcohol, 131–103°; isopropylbenzene, 149–130°; n-butylbenzene, 151–136°; and di-n-butyl phthalate, 200–179°. Measurements above 10^6 P were made by the pressure extrusion method, and those at lower viscosities by the gravity flow method. Knowledge of these viscosities, together with earlier information on the rates of decay of trapped free radicals in some of the glasses, indicates that macroscopic viscosity is not a major factor in determining such rates.

Introduction

Free radicals, cations, anions, electrons, and complexes produced photochemically or by ionizing radiation in organic glasses[2] decay at rates which depend on the nature and temperature of the trapping matrix and on the intermediate, but there is, as yet, no definitive knowledge as to what property or properties of the matrix control the decay rates. Thus, it is not known why the initial decay rate of ethyl radicals in 3-methylpentane (3MP) glass at 77°K (25% in ca. 3 hr) is much longer than that in methyltetrahydrofuran (MTHF) (25% in ca. 20 min), or why the half-life of the trapped electron varies from 16 min in 3MP at 77°K to several hours in either methylcyclohexane (MCH) or MTHF, or why some species trapped in 3MP glass are stable to higher temperatures than others.

One of the measurable physical properties of glasses with which decay rates of trapped intermediates might plausibly show a correlation is the viscosity. For this reason we have measured the viscosity of the frequently used glass matrices 3MP, MTHF, 2-methylpentane (2MP), and 2-methylpentene-1 (2MP-1) as a function of temperature over the experimentally accessible range up to about 10^{12} P (77°K for 3MP and 91°K for MTHF). Incidental to developing the techniques of measurement, we have extended the available viscosity data on n-propyl alcohol, isopropylbenzene, n-butylbenzene, and di-n-butyl phthalate.

Methods of determining viscosity in the ranges of interest in this work include the "pressure extrusion" method (10^6–10^{14} P),[3–7] the "gravity-fall" method (10^4–10^6 P),[7] the "sliding plate" method,[8] and the "concentric cylinder" method.[9–12] Empirical "penetration" viscometers, calibrated against known references, have also been used.[13–16] The only determination of the viscosity of organic glasses in the 77°K range of which we are aware is the investigation of Lombardi, Raymonda, and Albrecht[3] on mixtures of isopentane (IP) and 3MP at 77°K, employing the pressure extrusion technique used in the present work. Preliminary

work on this technique in our laboratory was initiated by R. F. C. Claridge and B. Wiseall.

Experimental Section

Method. The viscometer is illustrated in Figure 1. A cylinder of the desired organic glass, 0.5 to 3.5 cm high and 0.4 to 1 cm in radius, was frozen in the bottom of a precision bore glass or metal tube. A known pressure of helium was applied to the top of the plug, while the rate of extrusion of the meniscus at the bottom of the plug was observed through a cathetometer. From the pressure (P), the radius of the plug (R), the height of the plug (H), and the distance of the extrusion (L), as a function of time (t), the viscosity was calculated from the equation $\eta = PR^2t/4HL$. For samples in the viscosity range 10^4–10^6 P, extrusion occurred under

(1) This work has been supported in part by U. S. Atomic Energy Commission Contract AT(11-1)-1715 and by the W. F. Vilas Trust of the University of Wisconsin.

(2) For examples and references, see: (a) W. H. Hamill, "Ionic Processes in γ-Irradiated Organic Solids at −196°," a chapter in "Radical Ions," L. Kevan, Ed., John Wiley and Sons, Inc., New York, N. Y., in press; (b) J. E. Willard, "Radiation Chemistry of Organic Solids," a chapter in "Fundamentals of Radiation Chemistry," P. Ausloos, Ed., John Wiley and Sons, Inc., New York, N. Y., in press.

(3) J. R. Lombardi, J. W. Raymonda, and A. C. Albrecht, *J. Chem. Phys.*, **40**, 1148 (1964).

(4) E. C. Bingham and R. A. Stephens, *Physics*, **5**, 217 (1934).

(5) G. S. Parks, L. E. Barton, M. E. Spaght, and J. W. Richardson, *ibid.*, **5**, 193 (1934).

(6) C. M. Pittmann and R. N. Traxler, *ibid.*, **5**, 221 (1934).

(7) D. C. West, *Trans. Soc. Rheology*, **6**, 81 (1962).

(8) M. H. Aronson and R. C. Nelson, "Viscosity Measurement and Control," Instruments Publishing Co., Inc., Pittsburgh, Pa., Chapter 1.

(9) A. Pochettino, *Nuovo Cimento*, **8**, 77 (1914).

(10) H. L. D. Pugh, *J. Sci. Instr.*, **21**, 177 (1944).

(11) R. N. Traxler and H. E. Schweyer, *Proc. Am. Soc. Testing Materials*, **36**, 523 (1936).

(12) C. Mack, *J. Phys. Chem.*, **36**, 2901 (1932).

(13) R. N. J. Saal and G. Koens, *J. Inst. Petrol. Technol.*, **19**, 176 (1933).

(14) W. W. Pendleton, *J. Appl. Phys.*, **14**, 170, 551 (1943).

(15) S. M. Cox, *J. Sci. Instr.*, **20**, 113 (1943).

(16) H. Greenspan and E. Fischer, *J. Phys. Chem.*, **69**, 2466 (1965).
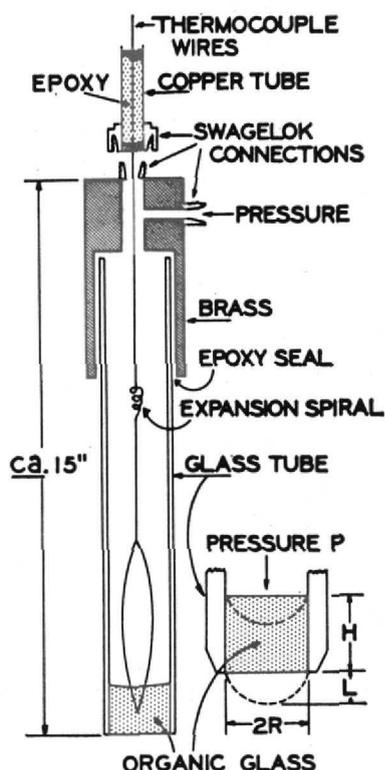
Figure 1. Viscometer tube.

the influence of gravity without the necessity of added pressure. Here the viscosity was calculated by the relation $\eta = \rho g R^2 t/4L$, where ρ is the density and g is the acceleration of gravity. The viscosity is given in poises when distances are in centimeters, time in seconds, the density in grams per cubic centimeter, and pressure in dynes per square centimeter. The limiting factors in the precision of the determinations were the measurements of L, H, P, and the temperature. L could be measured to ± 0.01 cm. H was measured from the low point of the meniscus of the upper surface of the glass to the flat lower surface of the glass. Since the equation used assumes a flat upper surface, and the depth of the meniscus was sometimes appreciable, this introduces an uncertainty. Pressures were measured to ± 2 psi between 10 and 100 psi and to ± 30 psi at pressures above 200 psi. The error from temperature measurements depended on the duration of the experiment, the difference between the temperature of the experiment and that of the reference junction of the thermocouple, and the value of $d\eta/dT$ for the particular compound. In the tabulations to follow, the temperatures are stated to the nearest 0.5°. For MTHF, η changed by about an order of magnitude per 2° at 90°K; for 3MP at 77°K the change was about an order of magnitude per 1°.

Formation of the organic glass in the bottom of the viscometer tube was accomplished by sealing a glass plate to the bottom of the tube with glycerol frozen at 77°K[3] and adding the liquid sample dropwise from a

pipet. When the glass cracked, warming it to just below the softening point (ca. 10^6 P) removed the cracks, and the plug could usually be recooled to the desired experimental temperature without recracking. At temperatures where the viscosity reached 10^{15} P or greater, recracking nearly always occurred.

A copper–constantan thermocouple frozen into the center of the glass plug monitored the temperature. Using a reference junction in liquid N_2 and a microvoltmeter with output to a chart recorder, the sensitivity was 3° per full scale in the 80°K region. The temperature of the liquid N_2 in the loosely sealed constricted-neck dewar used for the reference changed by less than 0.5°/24 hr relative to fresh liquid N_2 from a commercial tank.

The thermocouple wire passed out of the viscometer tube through a 0.25-in. i.d. copper tube. This was sealed at one end with a plug of heavy-grade epoxy cement and then filled with thin epoxy, which was allowed to harden, following which the second end was plugged with the heavy-grade epoxy.[17] If the outer insulation sheath was stripped from the portion of the double-stranded thermocouple wire which passed through the epoxy, the fitting was able to withstand at least 2600 psi without leaking, whereas when the outer insulation was not stripped, leakage occurred at pressures as low as 500 psi. A spiral in the thermocouple wire served as a spring to allow free movement when the glass sample was extruding.

Pressure was applied to the viscometer tube through a copper tube connected to a commercial helium tank. To minimize the warming resulting from compression of gas into the viscometer (as much as 15° at 1200 psi), the pressure was applied slowly, over a period of 3–5 min. The upper useful pressure was about 1200 psi. At higher pressures the plug usually broke loose, resulting in breakage of the glass tube and the surrounding dewar. Metal tubes did not break, but the glass plug was forced out at about the same pressure, even when the inside of the metal tube was threaded to a depth of 0.01 in. All experiments were conducted behind a metal shield with a heavy plastic window, through which the extrusion rate of the sample was observed with a cathetometer.

During operation, the viscometer tube containing the sample was clamped in a 0.5-l. unsilvered dewar flask. For measurements at 77.5°K, the flask was filled with liquid nitrogen. For temperatures above 77.5°K, a stream of gaseous nitrogen was used as the coolant. This was generated from liquid nitrogen by an electrical heater, passed through a coil of copper tubing immersed in liquid nitrogen, and then into the dewar containing the sample. The temperature was

controlled by the flow rate and by an auxiliary heater mounted on the copper feed tube between the cooling coil and entrance to the sample dewar. Liquid N_2 consumption for the range 100–77.5°K was from 5 to 20 l./hr. Styrofoam 2 in. in radius insulated the gaseous nitrogen feed tubes.

Penetration Viscometry. The methods of penetration viscometry were tested using rods with several shapes of point resting on a 3MP glass surface at 77°K. In each case the upper end of the rod was attached to a platform which carried a 10-kg load. Rounded ends ($^1/_4$–$^1/_8$-in. diam) and various pointed rods and needles were used. No indentation of the surface was observed in any case for times up to 6 hr.

Materials. All compounds tested were used as received. 3-Methylpentane (3MP), 2-methylpentane (2MP), and 2-methylpentene-1 (2MP-1) were Phillips Pure grade. Methyltetrahydrofuran (MTHF) and di-*n*-butyl phthalate (DBP) were Eastman White Label. Isopropylbenzene and *n*-butylbenzene were Aldrich laboratory grade, and the *n*-propyl alcohol was Fischer Certified grade.

Results

For each of the eight compounds and one mixture studied, viscosities were determined at temperature intervals of approximately 1°K from about 10^4 to 10^{12} P. For 3MP and *n*-C_3H_7OH (Tables I and II) several diameters of viscosity tube were used to test the effect

Table I: Determination of the Viscosity of 3-Methylpentane as a Function of Temperature Using Varied Sample Dimensions and Pressures

T, °K	Viscosity, P	R, cm	H, cm	P, psi	t, sec	L, cm
94.5	1.8×10^4	0.40	3.5	0	151	0.32^a
93.5	7.7×10^5	0.40	3.1	10	22	0.25
91.5	2.1×10^6	0.40	2.6	10	47	0.24
90.5	1.9×10^5	0.90	2.4	0	720	0.76^a
90.5	2.5×10^5	0.40	3.5	20	113	0.37
90.0	1.1×10^7	0.40	1.6	40	28	0.18
88.5	3.5×10^7	0.40	3.0	20	540	0.29
88.5	1.0×10^8	0.90	1.9	250	31	0.56
87.0	5.2×10^7	0.90	3.1	49	125	0.53
85.5	1.5×10^8	0.72	2.0	10	1,276	0.30
85.5	1.8×10^8	0.90	3.2	40	408	0.40
84.5	3.3×10^8	0.90	2.6	49	240	0.19
84.5	6.4×10^8	0.90	2.4	500	116	0.53
83.0	2.3×10^9	0.72	0.9	42	900	0.16
83.0	1.5×10^9	0.90	3.0	500	240	0.37
82.0	2.1×10^{10}	0.90	2.2	500	1,042	0.16
80.5	3.8×10^{10}	0.90	1.3	1000	810	0.23
79.5	1.7×10^{11}	0.90	2.2	1000	6,090	0.22
77.5	1.2×10^{12}	0.90	0.5	500	5,820	0.07
77.5	1.9×10^{13}	0.95	2.5	1000	27,000	0.09^b
77.5	2.6×10^{12}	0.95	2.5	1200	41,000	0.12^b

^{a} Gravity-fall method. Density assumed to be 1.0 g cc^{-1}.
^{b} Metal viscometer tube used.

Table II: Determination of the Viscosity of *n*-Propyl Alcohol as a Function of Temperature^a

T, °K	Viscosity, P	R, cm	H, cm	t, sec	L, cm
131.0	1.9×10^4	0.72	2.1	34	0.21
130.0	4.3×10^4	0.31	3.4	237	0.12
128.5	7.9×10^4	0.31	4.9	925	0.25
128.5	5.8×10^4	0.55	3.2	77	0.09
127.5	6.9×10^4	0.55	3.1	92	0.09
127.0	8.0×10^4	0.55	3.1	403	0.34
126.5	1.8×10^5	0.31	4.8	1007	0.12
126.0	1.4×10^5	0.55	3.1	397	0.19
125.5	1.7×10^5	0.72	2.4	222	0.15
125.0	1.9×10^5	0.55	3.5	720	0.25
125.0	2.1×10^5	0.72	1.5	359	0.20
124.5	1.5×10^5	0.72	2.5	458	0.36
124.0	1.6×10^5	0.72	2.9	540	0.39
123.5	2.4×10^5	0.72	3.6	498	0.24
122.0	4.9×10^5	0.90	3.4	487	0.18
121.0	7.1×10^5	0.90	3.2	1140	0.29
120.0	1.0×10^6	0.90	3.4	1182	0.22
119.5	5.7×10^5	0.90	3.1	573	0.18
119.0	1.2×10^6	0.90	3.1	1092	0.17
119.0	1.4×10^6	0.90	3.1	292	0.04
117.5	3.2×10^6	0.90	1.8	2134	0.12
115.5	1.1×10^7	0.90	4.8	33	0.17
112.5	2.4×10^7	0.90	3.3	30	0.21
109.0	2.0×10^8	0.90	5.9	392	0.33
103.5	1.5×10^{10}	0.90	1.5	6166	0.26

^{a} All determinations except those at 115.5°K and below were made by the gravity-fall method, using 0.91 g cc^{-1} as the value of the density in making the calculations. This was determined in an experiment at 100°. The pressures used at 115.5, 112.5, 109, and 103.5° were 20, 40, 70, and 70 psi, respectively.

of this variable and to extend the range of measurement. All other determinations (Table III) were made with tubes of 0.90-cm radius.

The fact that samples were solidified at low temperatures before exposure to high pressure gas, and that the results are in agreement with those obtained by other methods in earlier work, when similar temperatures were used, supports the assumption that the measured viscosities were not affected by the presence of dissolved helium.

Attempts to measure the viscosities of C_2H_5I, *n*-C_3H_7I, *n*-C_4H_9I, and MCH glasses were unsuccessful because samples of the necessary size always crystallized. Samples of MCH could be frozen to a glass in the smaller diameter viscosity tube (0.31-cm radius) by very rapid cooling, but the glass was always badly cracked and had a severely deformed meniscus. Attempts to remove the cracks by warming produced crystallization.

Discussion

Correlation and Extrapolation of Data. For comparing our data with data at lower viscosity from the literature and for convenience in extrapolating the data to higher viscosities, we have plotted log η *vs.* T^{-1} in

Table III: Viscosity of 2-Methylpentane, 2-Methylpentene-1, 2-Methyltetrahydrofuran, Isopropylbenzene (iPB), n-Butylbenzene (nBB), and Di-n-butyl Phthalate (DBP) as a Function of Temperature and of 3-Methylpentane-Isopentane (3MP-iP) Mixtures as a Function of Composition

T, °K	Viscosity, P	T, °K	Viscosity, P	T, °K	Viscosity, P
A. 2MP[a]		**B. 2MP-1**[b]		**C. MTHF**[c]	
96.5	5.2×10^4	102.5	1.0×10^4	107.5	2.1×10^3
95.5	7.5×10^4	100.0	1.4×10^5	105.5	3.3×10^3
94.5	2.2×10^5	98.5	7.1×10^5	101.5	4.5×10^6
93.5	3.3×10^6	96.5	3.6×10^6	99.5	1.8×10^7
92.5	2.5×10^6	95.5	7.4×10^6	97.5	1.8×10^8
91.5	5.9×10^6	94.5	8.0×10^7	96.0	3.0×10^8
91.0	8.2×10^6	93.5	5.7×10^7	95.5	2.5×10^8
90.5	7.3×10^6	92.5	2.9×10^8	94.5	5.5×10^8
89.5	2.9×10^7	91.5	5.4×10^8	93.5	4.0×10^9
88.5	5.0×10^7	90.5	1.2×10^9	93.0	9.6×10^9
87.5	1.0×10^8	90.0	3.1×10^9	92.5	1.6×10^{10}
86.5	3.8×10^8	88.0	3.5×10^{10}	92.0	1.5×10^{11}
86.0	8.7×10^8				
85.0	1.7×10^9	**E. nBB**[d]		**F. DBP**[e]	
84.5	4.4×10^9	151.0	6.6×10^3	200.0	3.4×10^5
81.5	1.2×10^{11}	146.5	1.6×10^5	199.5	3.2×10^5
80.5	6.3×10^{11}	139.5	8.6×10^6	196.0	1.7×10^6
		136.0	4.3×10^8	194.5	3.5×10^6
D. iPb[d]				191.0	1.0×10^7
149.0	6.6×10^3	3MP, vol. fract[f]	Viscosity, P	189.0	5.0×10^7
143.5	3.4×10^5			187.0	2.6×10^8
139.5	7.4×10^6	**G. 3MP-iP at 77.5°K**		184.0	4.6×10^8
136.5	7.1×10^7	1.00	2.2×10^{12}	182.0	9.2×10^8
130.0	5.5×10^{10}	0.89	2.8×10^{11}	181.5	1.3×10^9
		0.80	1.3×10^{11}	179.5	9.6×10^9
		0.67	1.3×10^{10}		
		0.25	3.7×10^7		

[a] Formed good glass on freezing at 77°K. [b] Cracks removed by annealing at 98-99°K after freezing at 77°K. [c] Cracks removed by annealing at 100-101°K after freezing at 77°K. [d] Viscosities of less than 10^6 P determined by gravity-fall method, using density values of ref 18. [e] Solid CO_2 ($T = 194.5$°K) used as temperature of reference junction of thermocouple. [f] Volume of 3MP/(volume of 3MP + volume of iP).

Figures 2-4. For those compounds for which liquid state viscosity data are available (n-propyl alcohol[18-20] [Figure 2] and the alkyl benzenes and dibutyl phthalate[21] [Figure 3]), the new data on glasses all fall on smooth curves continuous with the liquid phase data, indicating that the different methods of measurement are mutually consistent. (The trend of our points for n-propyl alcohol, obtained by the gravity-fall method, to deviate from the curve as the temperature increases toward 130°K may be due to the fact that the density at 100° was used for the calculations throughout this region.) At viscosities above about 10^4 P (i.e., at temperatures below the glass "softening" temperature) the plots of Figures 2-4 all approximate to straight lines. However, since the accessible range of measurement which they cover is only about 15°, and since the glass transition temperature is probably only slightly below the minimum temperature used in each case (i.e., at viscosities of about 10^{13} P),[22] it is improbable that the viscosities at lower temperatures are accurately predictable by linear extrapolation. It is to be

expected that such predictions will be low, but it is reasonable to assume that relative values for different compounds will be qualitatively correct.

For 3MP, 2MP, 2MP-1, and MTHF, which are currently of interest as matrices in radiation chemistry studies, the parameters in the equation $\log \eta = AT^{-1} + B$ have been determined by a least-squares fit of the data. Table IV shows the values of A and B for each compound, the experimental temperature range from which the data were derived, the calculated viscosities at 77.5°K, assuming that the extrapolation is valid

(18) T. E. Thorpe and J. W. Rodger, *Phil. Trans. Roy. Soc. London*, **A185**, 397 (1894).

(19) G. Tamman and W. Hesse, *Z. Anorg. Allgem. Chem.*, **156**, 245 (1926).

(20) D. J. Denney, *J. Chem. Phys.*, **30**, 159 (1959).

(21) A. J. Barlow, J. Lamb, and A. J. Matheson, *Proc. Roy. Soc.* (London), **A292**, 322 (1960).

(22) For examples and references, see B. Wunderlich, *J. Phys. Chem.*, **64**, 1052 (1960); M. R. Carpenter, D. B. Davies, and A. J. Matheson, *J. Chem. Phys.*, **46**, 2451 (1967).
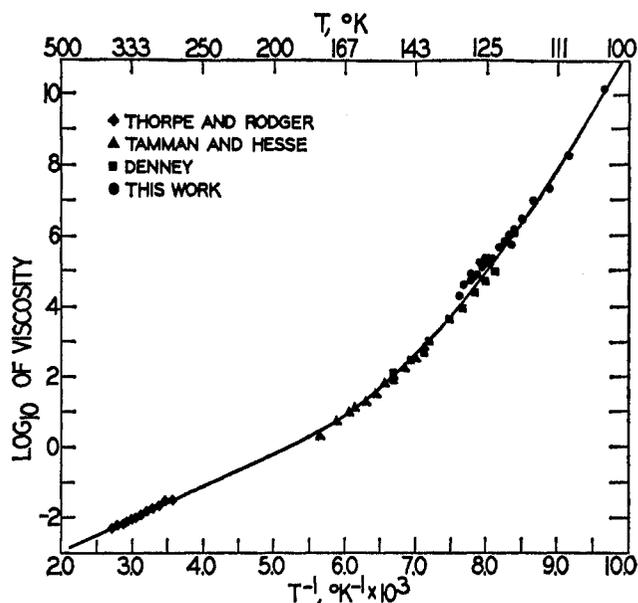
Figure 2. Temperature dependence of viscosity (poises) of n-propyl alcohol liquid and glass.
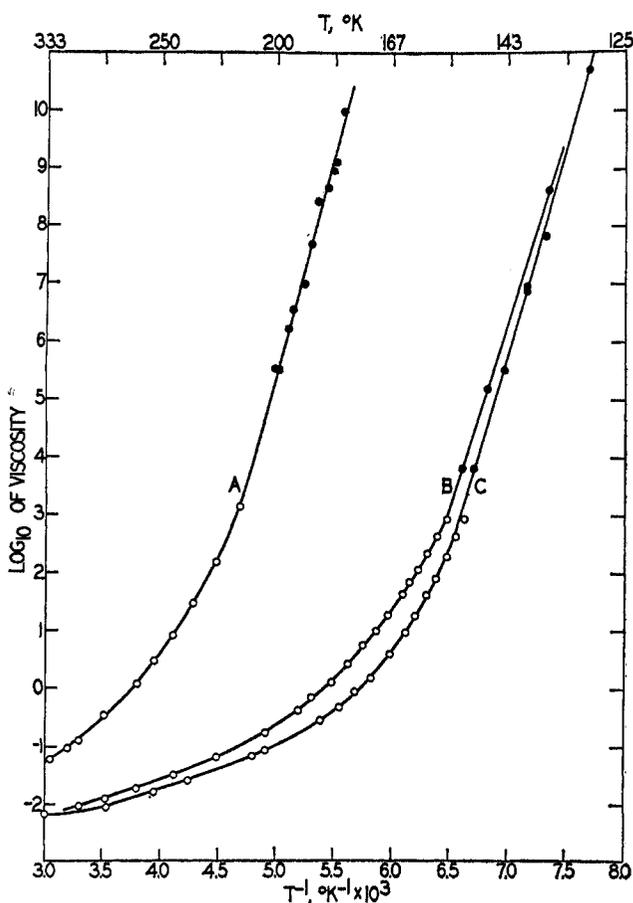
Figure 3. Temperature dependence of viscosity (poises) for some cyclic organic compounds in their liquid and glassy states:
A, di-n-butyl phthalate; B, isopropylbenzene (cumene);
C, n-butylbenzene; O, Matheson, et al.; ●, this work.

(η for 3MP is the measured value), and the Arrhenius E factors.
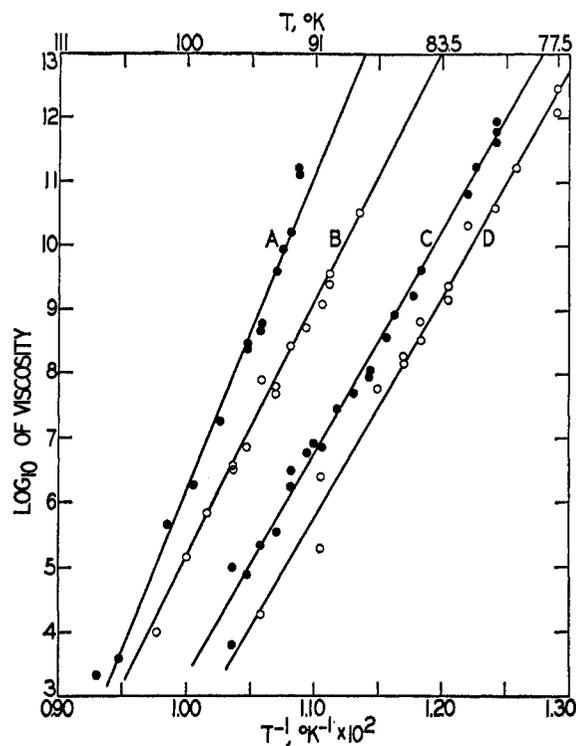
Figure 4. Temperature dependence of viscosity (poises) for some organic glasses used as radiation matrices:
A, 2-MTHF; B, 2MP-1; C, 2MP; D, 3MP.

Table IV: Viscosity–Temperature Relationships of Some Glasses Commonly Used as Trapping Matrices

Compound	Viscosity at 77.5°K, P[a]	E, ev	A, °K × 10^{-3}	B	T range, °K
3MP	2.2×10^{12}	0.69	3.46	−32.2	94.5–77.5
2MP	2.4×10^{13}	0.69	3.48	−31.5	96.5–80.5
2MP-1	3.8×10^{16}	0.72	3.96	−34.3	102.5–88
2MTHF	3.7×10^{20}	0.98	4.93	−43.1	107.5–92

[a] Extrapolated for all compounds except 3MP.

The viscosities of 3MP–iP mixtures obtained in the present work (Table III-G) and by Lombardi, Raymonda, and Albrecht[3] are plotted in Figure 5. There is good agreement within the precision of the experiments. The average value for our three measurements in pure 3MP is a little more than double that obtained from the relation $\log \eta = 5.95 + 6X_{3MP}$, obtained[3] from measurements on mixtures containing 0.8 and less volume % 3MP.

An approximate estimate of the viscosity for methylcyclohexane (MCH) can be made despite the fact that it cannot be measured because of cracking and crystallization. When glasses are formed at 77.5°K by direct immersion in liquid nitrogen, those with extrapolated viscosities greater than about 10^{15} P at this temperature (2MP-1, ca. 10^{16} P; MTHF, ca. 10^{20} P) invariably crack, while those of lower viscosity (isopentane, ca. 10^{6} P;
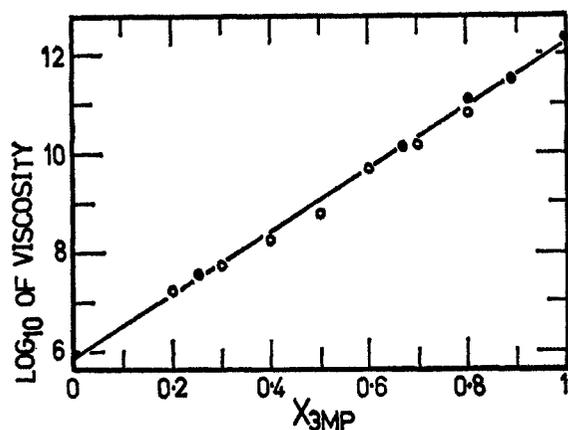
Figure 5. Viscosity (poises) of 3MP–iP mixtures at 77°K as a function of volume fraction (X_{3MP}): O, data of Lombardi, Raymonda, and Albrecht; ●, present work.

3MP, ca. 10^{12} P; 2MP, ca. 10^{13} P) all form stable glasses. The extent of cracking, and the length of time before cracking commences after formation of the glass, also depends on the viscosity. This is indicated by the fact that MTHF, the alkyl benzenes, and di-n-butyl phthalate ($\eta \geq 10^{20}$ P at 77.5°K) all show severe cracking within seconds of formation, while 2MP-1 ($\eta = ca. 10^{16}$ P) often does not crack for several minutes, and then does so to a limited extent. The glasses that crack can be converted to the uncracked state by warming to a temperature where η is about 10^6 P. If such a glass is then cooled slowly by nitrogen vapor, cracks again appear spontaneously at a temperature corresponding to approximately 10^{15} P, and the cracking becomes worse as the temperature is lowered further. MCH exhibits behavior rather similar to MTHF. A glass can be formed by extremely rapid cooling, but this soon cracks extensively. This may imply that its viscosity is similar to that of MTHF, and, by comparison with 2MP-1, it seems probable it is not less than 10^{16} P. This conclusion is further substantiated by evidence[23] that the addition of MCH to iP or 3MP raises the viscosity, coupled with the evidence of Figure

5 that viscosity–composition relationships are approximately linear. Assuming such linearity, the Rosengren[23] data imply that the viscosity of MCH at 77.5°K is about 10^{17} P if E is assumed to be 0.7 eV, or 10^{21} P if $E = 1.0$ eV.

Meniscus Effect. The points for 3MP in Figure 4 include the determinations using the gravity-fall method (Table I) and all those using the pressure-extrusion method with the 0.95-, 0.90-, and 0.72-cm radius tubes.

The 3MP points obtained with smaller diameter tubes all fell on a line close to the 2MP line of Figure 4. The deviation of these points in the direction of higher viscosity is ascribed to the difficulty of estimating the sample height, H, where there is a very pronounced meniscus. Measurement was made from the bottom of the meniscus to the bottom of the plug. In the smallest tubes the meniscus was sometimes several millimeters deep. The larger the internal radius of the viscosity tube, the smaller was this error. For the gravity-fall method, H does not enter into the calculation of η, and no such error is introduced.

Decay of Radiation-Produced Reaction Intermediates. Ethyl radicals produced by dissociative electron capture[24,25] in 3MP glass at 77°K, using electrons produced by γ irradiation or by photoionization of tetramethyl-p-phenylenediamine, decay by 25% in 3 hr. The corresponding decay time in MTHF is about 20 min.[25] The data of Figure 4 show that the viscosity of MTHF at 77°K must be orders of magnitude higher than that of 3MP, demonstrating dramatically that the molecular relaxation processes necessary to allow the radical decay reaction are not closely related to the molecular properties responsible for the macroscopic viscosity.

(23) Kj. Rosengren, *Acta Chem. Scand.*, 16, 1421 (1962).

(24) R. F. C. Claridge and J. E. Willard, *J. Am. Chem. Soc.*, 87, 4992 (1965).

(25) M. Shirom and J. E. Willard, *J. Phys. Chem.*, 72, 1702 (1968).