Viscosities of Moderately Concentrated Solutions of Polyethylene in Ethane, Propane, and Ethylene

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Synopsis

The viscosities of moderately concentrated solutions of low-density polyethylenes in ethane, propane, and ethylene have been measured at low shear rate in the temperature range of 150–250°C and in the pressure range of about 15000–30000 psi. Within the precision of the measurements, the relative viscosity is independent of pressure over the range investigated but increases as the solvent is changed from propane through ethane to ethylene. The activation energy for the relative viscosity in ethane varies from about 0.5 to 2.5 kcal/mole as the concentration changes from 5 to 15 g/dl. Effects of polymer concentration and molecular weight on solution viscosity in ethane at 150°C have been determined, and all of the data can be represented by a single straight-line plot of the logarithm of relative viscosity versus the intrinsic viscosity (in *p*-xylene at 105°C) times concentration. This simple relation is valid over wide ranges of polymer concentration and molecular weight and over more than two orders of magnitude of relative viscosity. The solution viscosities of the polyethylenes in the three supercritical fluid solvents used appear surprisingly low at first sight. This behavior is partly a result of the low solvent viscosities but also might mean that the polymer has an abnormally low segmental friction factor compared to that in solutions under more familiar conditions.

INTRODUCTION

It has been established that, at sufficiently high pressures, liquid polyethylene is miscible in all proportions with alkanes of low molecular weight[1] and with ethylene.[2-4] The polymer may be said to dissolve in the compressed fluid solvent, regardless of whether the latter is a condensable "vapor" or an uncondensable "gas" above its critical temperature.

A knowledge of the viscosities of these solutions at moderately high polymer concentrations was likely to be of interest for two reasons. New information would be made available on the viscosity behavior of polymers in solvents of low density under unfamiliar conditions. In addition, some of the data would be obtained under conditions closely resembling those existing in high-pressure polymerizations of ethylene and, therefore, prob-

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ably would allow improved calculations of reactor performance.

This paper will report on the viscosities of solutions of low-density polyethylene (LDPE) in ethane, propane, and ethylene, obtained with a rolling-ball viscometer operated at low shear rate, in the temperature range of 150–250°C and in the pressure range of about 15000–30000 psi.

EXPERIMENTAL

Equipment and Procedure

The theory of the rolling-ball viscometer has been discussed quite thoroughly by Hubbard and Brown,[5] and the reader is referred to their paper for details. The same authors also performed a very careful experimental study and defined the conditions under which streamline conditions exist in this instrument. Using dimensional analysis, together with their experimental data, they were able to derive an expression for the absolute viscosity in terms of the angle of inclination of the viscometer tube, the roll velocity of the ball, densities of fluid and ball, and the instrument geometry. This analysis enables one to choose the proper instrument for the desired viscosity range without prior experimentation. The final expression obtained by Hubbard and Brown for the viscosity is

$$\eta = (5\pi K/42V)g \sin \theta (\rho_s - \rho) \, d(D + d) \qquad (1)$$

where η is the viscosity (in poise), V is the roll velocity of the ball (in cm/sec), g is the acceleration due to gravity (980 cm/sec²), θ is the angle of inclination of the axis of the cylindrical viscometer tube from the horizontal, ρ_s is the ball density (in g/cm³), ρ is the fluid density (in g/cm³), D is the inside diameter (ID) of the viscometer tube (in cm), d is the diameter of the ball (in cm), and K is a dimensionless correlation factor which is a function[5] of d/D only.

Equation (1) is valid in the streamline region only. The correlation factor K was plotted by Hubbard and Brown over the approximate range of d/D of 0.85–0.99. Assuming the values of d, D, ρ_s and ρ to be constant and known, we may write

$$\eta = C' \sin \theta / V \qquad (2)$$

where C' now can be obtained from Hubbard and Brown's values of K together with the knowledge of the fixed values of d, D, ρ_s and ρ under a given set of experimental conditions.

The measurements to be discussed were performed under conditions where the experimental error caused by factors other than an imperfect calibration of the instrument was probably not less than ±10% in the more favorable cases and about ±20% in most others. It seemed reasonable to assume, therefore, a constant value for the solution density ρ, although this quantity varied somewhat with the concentration of the solution. Only two ball diameters were used ultimately. These diameters, the other parameters chosen, and the resulting values of C' are listed in Table

TABLE I
Conditions of Rolling-Ball Measurements and the Calibration Constants C'

| | Ball characteristics | | | |
Type	Density ρ_s, g/cm^3	Diameter d, cm	d/D[a]	C'[b]
Small[c]	7.65	0.945	0.85	2.25
Medium[d]	8.52	1.057	0.95	0.291

[a] The ID of the viscometer tube D was 1.110 cm.
[b] The density of the solutions was 0.60 g/cm^3.
[c] These balls were made of ingot iron.
[d] These balls were made of Mu metal.

I.   The uncertainties in the values of C', which arise from irregularities in the ID of the viscometer tube, are less than about $\pm 5\%$. The values of C' were checked via measurements on aqueous glycerol solutions of known viscosity.

From their experimental work, Hubbard and Brown determined a critical Reynolds number Re_c below which streamline flow was observed. The value of Re_c was found to be 10 for $d/D = 0.85$ and 15 for $d/D = 0.95$. For the instrument used here, $Re = 0.5V\rho/\eta$. At viscosities exceeding 5 Cp, streamline conditions were always maintained in our experiments according to the above criterion.   In the range of 2–5 Cp, where marginal conditions of flow sometimes prevailed, tests always were made in order to insure that the calculated viscosity was independent of the angle of roll which, in general, was maintained between 2° and 8°.   According to Hubbard and Brown, Re has to exceed Re_c by a factor of about two before deviations from streamline flow are sufficiently severe to introduce an appreciable correction into the viscosity calculated by eqs. (1) or (2).   No data obtained under such conditions will be cited in this work.   Using the present equipment with polyethylene solutions in supercritical fluids, and in low-pressure measurements of polystyrene dissolved in benzene (made as an additional check), there was no evidence of an angle-dependent viscosity up to several times the critical Reynolds number found by Hubbard and Brown.   There appears to be adequate evidence, therefore, that all data to be reported in this paper were obtained under Newtonian conditions.

Equipment and Procedure

The physical arrangement of the viscometer is illustrated by Figure 1. The viscometer tube A extending between reducer couplings M was mounted at one end in a trunnion block K.   The viscometer tube could be inclined through angles of about $\pm 15°$ from the horizontal by means of a steel cable B attached at one end to the end closure N and proceeding via pullies through the barricade wall to a spool on a d-c motor fitted with reversing switches.   The viscometer tube, made of 316 stainless steel with a yield strength of 1×10^5 psi, had a $^3/_4$ in. outside diameter (OD), a
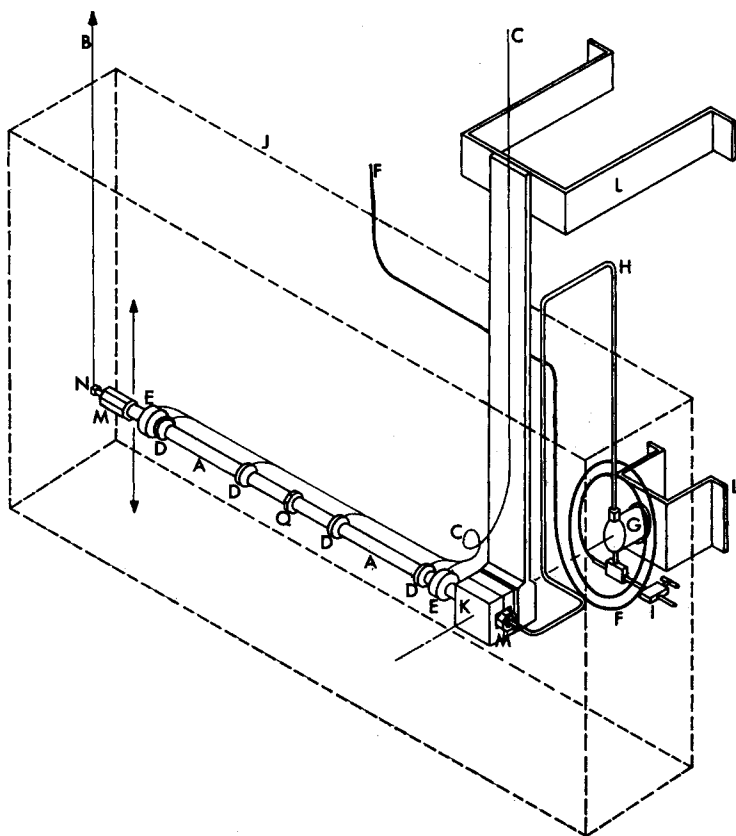
Fig. 1. Physical arrangement of rolling-ball viscometer: (A) the high-pressure vis-cometer tube; (B) a steel cable leading to spool on d-c motor; (C) Teflon-insulated wires leading to impedance bridge and power supply for electromagnets; (D) sensing coils; (E) electromagnet coils; (F) $1/8$ in. OD high-pressure tubing leading to strain gauge and filling system; (G) rupture disk mounted in a ball bearing; (H) $1/4$ in. OD high-pressure arm tubing; (I) venting valve; (J) oil bath (in raised position); (K) trunnion block; (L) supports on barricade wall; (M) reducer couplings; (N) end closure; (Q) weld with hexagonal faces for assembly and disassembly of instrument.

$7/16$ in. ID, and was about 20 in. long. The internal volume of the vis-cometer was 50 cm^3 between the reducer couplings M. It was found that diffusion into the $1/4$ in. OD arm tubing H was negligible, so that the volume of the instrument was taken to be 50 cm^3. The maximum safe working pressure of the viscometer tube p_w, calculated by the formula of Moore and Opersteny,[6] was about 33000 psi. In the first instruments used, some yielding at the weld Q in the center of the viscometer tubes actually took place at lower pressures. The weld then was replaced by silver-solder, and the instrument was found to be quite adequate in routine measurements up to 30,000 psi.

Balls with d/D of 0.85 and of 0.95 were eventually used in all measure-

ments. The smaller ball is more desirable, because the roll time is a great deal less sensitive to changes in d/D brought about by irregularities in the ID of the viscometer tube, pressure, or any differential expansions effects. Wherever possible (at sufficiently high viscosity), measurements were performed with the small balls. However, checks between the "small-ball" and "medium-ball" viscosities were satisfactory, and it was not necessary to consider variations in d/D brought about by any of the factors mentioned above. Large balls, with d/D of 0.98, were not satisfactory, apparently because of mixing difficulties.

The viscometer tube was fitted with four sensing coils D, allowing the roll time to be taken over three sections of the tube. This provided a good check on the uniformity of the solution and the attainment of equilibrium conditions. The coils were wound on copper forms, and each consisted of about 100 turns of No. 30 Teflon-insulated (Tufflon) wire having a d-c resistance of 2.5–3 ohm. Motion of the ball through each coil was sensed by the electrical imbalance on a Brush recorder (Strain Analyzer Model 3L310), making use of an impendance bridge of which the viscometer coils (pairwise) formed two arms. The electromagnet coils E, originally designed to hold the ball in position while the tube was being inclined at the desired angle, were never used, because without these devices, there was always sufficient time for the ball to attain a constant velocity by the time it had rolled through the first sensing coil.

All of the coils were in fixed positions with respect to each other and with respect to a given element in the viscometer tube. These positions were fixed by use of set screws through thin interconnecting copper sleeves. When the viscometer was disassembled for cleaning, all of the coils with the connecting wires could be removed in two rigid sections.

The LDPE solutions in ethylene and in other supercritical fluids were made simply by placing a known weight of polymer into the viscometer tube and then freezing the calculated amount of gas into the viscometer as described earlier.[7]

After the viscometer had been submerged in the oil bath J (by raising the latter), a period of one-half to several hours, depending on the polymer concentration, melt index and intensity of mixing, was required before the ball could be observed to roll through all four sensing coils. Even after uniform roll velocity had been attained, the apparent viscosity usually decreased over a period of 4–5 hr after immersion before a constant viscosity was attained. Although some polymer degradation often occurred during this period, virtually all of this apparent viscosity decrease was caused by the dissolution of the polymer film (formed during initial mixing) off the walls of the viscometer tube. Although viscosities had, in general, reached an essentially constant value 4–5 hr after immersion of the viscometer in the oil bath, most of the viscosity measurements reported here were taken 16–24 hr after immersion.

The various polyethylene samples used in this study are described in Table II.

TABLE II
Description of LDPE Samples Used

Designation	Melt index[a]	Intrinsic viscosity $[\eta]$, dl/g[b]	$\bar{M}_v$[c]
Type A	25	0.70	28,000
Type B	3	0.90	45,000
Type C	0.3	1.11	64,000
Fraction 2 $(\bar{M}_n = 250\,000)$[d]		1.98	230000

[a] Determined via *ASTM* Method D 1238-65T, conditions FR-E.

[b] Measured in *p*-xylene at 105°C.

[c] Viscosity-average molecular weight calculated from $[\eta]$ according to Trementozzi.[8]

[d] The number-average molecular weight $\bar{M}_n$ is higher than $\bar{M}_v$ for this fraction, apparently because of the effect of long-chain branching on $[\eta]$.

RESULTS

It became clear during the early phases of this work that the largest error was likely to be introduced by unknown changes in the polymer concentration and molecular weight brought about by polymerization and polymer degradation. Polymerization can, of course, be avoided by operating in solvents other than ethylene, whereas degradation can be minimized by operating at low temperatures. Thus it appeared that it would be easiest to obtain a clear description of the separate effects of temperature, pressure and solvent on the solution viscosity by first obtaining data in a nonpolymerizing solvent at a relatively low temperature.
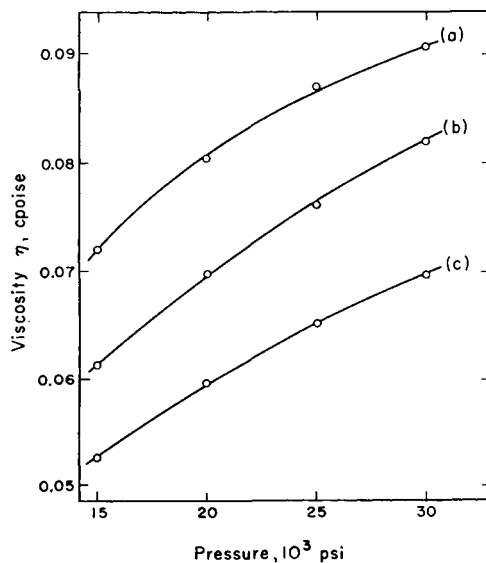

Fig. 2.   Viscosity of ethane vs. pressure at (a) 150°C; (b) 200°C; (c) 250°C.

As will be demonstrated, the variable most useful in correlating all data in the form of a simple expression is the relative viscosity η_r; i.e., the solution viscosity η divided by the solvent viscosity η_0. The solvents chosen for this study, other than ethylene, were ethane and propane. Polyethylene solutions in these three solvents were expected to have similar viscosities. Graphs then were prepared for the pressure and temperature dependencies of the viscosity of ethane (Fig. 2) and of ethylene (Fig. 3) from the reduced variable correlation of Carr et al.[9], and of propane (Fig. 4) from the direct experimental measurements of Starling et al.[10]

The effects of pressure and solvent on the solution viscosity are revealed by the data in Table III. Recognizing the fact that the reproducibility of these data is not better than about ±10%, we conclude that η_r is, within
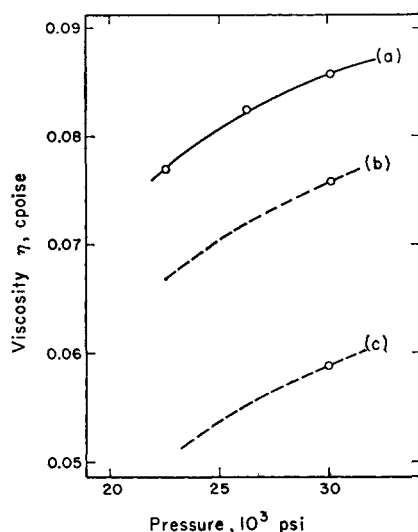

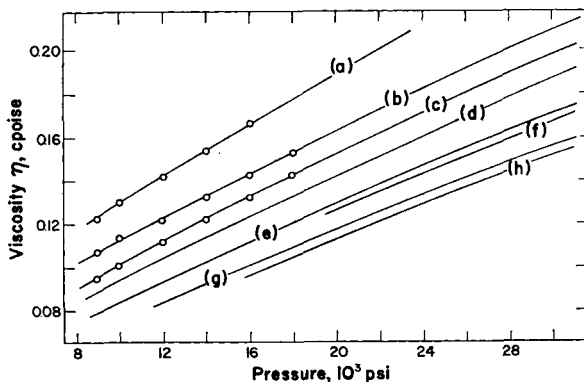Fig. 3.   Viscosity of ethylene vs. pressure at (a) 150°C; (b) 200°C; (c) 250°C.

Fig. 4. Viscosity of propane vs. pressure at (a) 93.3°C; (b) 121°C; (c) 149°C; (d) 171°C
(e) 204°C; (f) 211°C; (g) 238°C; (h) 250°C.

TABLE III
Effects of Pressure and Solvent on Solvent and Solution Viscosity,
Type A LDPE at 10 g/dl and 150°C

Pressure, 10^3 psi	Solvent	Viscosities		
		Solution η, Cp	Solvent η_0, Cp	Relative η_r
15.8	Propane	8.6	0.132	65.2
16.3	Propane	9.0	0.134	67.3
18.8	Propane	9.6	0.147	65.3
19.0	Propane	13.0	0.148	87.9
23.0	Propane	11.2	0.167	67.1
24.0	Propane	11.2	0.171	65.5
18.3	Ethane	6.6	0.79	83.5
18.7	Ethane	6.9	0.79	87.3
22.2	Ethane	7.3	0.83	88.0
23.0	Ethane	7.3	0.84	86.9
27.0	Ethylene	8.8	0.83	106
27.1	Ethylene	9.1	0.83	110
27.6	Ethylene	11.2	0.89	133
28.1	Ethylene	11.5	0.89	137

experimental error, independent of pressure over the range investigated (i.e., the pressure dependence of η is the same as that of η_0) and that η_r increases as the solvent is changed from propane through ethane to ethylene. Since the effects on the viscosity of changing the solvent can be estimated, it is best to calculate the viscosities of the ethylene solutions from the data obtained for the ethane solutions.

Recovery of the polymer after the measurements of Table III gave polymer weight losses which generally were in the range of 4–8% of the polymer charged. With the other LDPEs, weight losses (or gains) often were somewhat greater and less reproducible. Within the accuracy required for this work, it is legitimate to
assume that the polymer concentration during an experiment is given by the initial polymer concentration.

In order to evaluate the temperature coefficients of the viscosity, it was necessary to use solvents other than ethylene; a small, progressive amount of polymerization nearly always occurred in ethylene at the elevated temperatures. Since all systems were relatively stable toward any degradation after several hours exposure to the bath temperatures, meaningful values of an activation energy for viscous flow could be obtained by making measurements at the highest temperature first, after nearly all degradation had ceased, and then lowering the temperature. This procedure gave, of course, a pressure decrease throughout each experiment. Since, however, η_r was pressure-independent, the significant quantity, an energy of activation for η_r, could be obtained from these experiments (Tables IV and V). The activation energy E_a is seen to be concentration-dependent, but always small, as expected for a system with an extraordinarily large free volume.[11]

TABLE IV

Effect of Temperature on the Viscosities

LDPE Type	Solvent	Concn c, g/dl	Pressure, 10³ psi	Temp, °C	Viscosities		
					Solution η, Cp	Solvent η₀, Cp	Relative η_r
A	Propane	10	22.0	155	11.0	0.160	68.9
A	Propane	10	27.0	212	9.5	0.159	53.8
B	Propane	10	23.5	150	32	0.168	191
B	Propane	10	28.6	212	23	0.163	135
B	Ethane	10	22.0	150	14.2	0.077	185
B	Ethane	10	27.0	210	10.7	0.069	155
A	Ethane	15.0	20.5	100	49	0.093	530
A	Ethane	15.0	21.0	106	46	0.092	500
A	Ethane	15.0	21.4	110	44	0.091	480
A	Ethane	15.0	22.0	120	38	0.090	420
A	Ethane	15.0	23.0	130	35	0.088	400
A	Ethane	15.0	25.3	152	29	0.087	330
A	Ethane	15.0	16.4	152	28	0.075	370
A	Ethane	15.0	20.5	210	17	0.068	250
A	Ethane	10.0	19.0	121	9.8	0.092	106
A	Ethane	10.0	21.0	152	8.3	0.083	100
A	Ethane	10.0	25.5	213	6.2	0.073	85
A	Ethane	6.0	18.0	123	2.1	0.083	25.3
A	Ethane	6.0	20.6	153	1.9	0.081	23.5
A	Ethane	6.0	25.0	218	1.7	0.072	23.6

Because of the small values of E_a, it seems permissible to identify activation energies for the ethylene solutions with those observed for the ethane and propane solutions.

TABLE V
Activation Energy for Viscous Flow (for η_r)

LDPE type	Solvent	Concn c, g/dl	Activation energy E_a, kcal/mole
A	Ethane	6	0.2
A	Propane	10	1.7
B	Propane	10	2.2
B	Ethane	10	1.2
A	Ethane	10	1.0
A	Ethane	15	2.4

TABLE VI
Viscosity of Ethane Solutions at 150°C

LDPE	Pressure, 10^3 psi	Concn c, g/dl	Viscosity η, Cp Exptl	Viscosity η, Cp Averaged[a]
Type A	21.1	6	2.8	2.5
Type A	21.5	6	2.2	
Type A	23.0	10	7.3	
Type A	22.2	10	7.3	
Type A	18.7	10	6.9	7.3
Type A	18.3	10	6.6	
Type A	21.0	10	8.3	
Type A	23.0	15	30	
Type A	16.4	15	28	28
Type A	25.3	15	29	
Type A	22.4	20	105	109
Type B	19.9	6	3.5	4
Type B	22.0	10	14.2	
Type B	25.0	10	17	17
Type B	21.2	10	19	
Type B	23.2	15	190	107
Type B	23.8	20	470	660
Type C	22.0	3	1.4	1.8
Type C	23.8	4	2.2	2.6
Type C	23.5	6	7.5	
Type C	22.4	6	4.7	5.8
Type C	24.5	6	8.4	
Type C	21.8	10	30	28
Type C	23.9	10	23.1	
Type C	23.5	15	360	205
Type C	25.0	20	~1000	1480
Fraction 2	23.0	3	2.3	2.3
Fraction 2	21.0	4	9	9
Fraction 2	19.0	6	45	45
Fraction 2	23.4	8	480	480

[a] These averaged values are the least-squared values from the appropriate plots in Fig. 5.

Having evidence that changes in temperature, pressure and solvent can be accounted for, it seems in order to investigate the effects of polymer concentration and molecular weight in a system where no polymerization occurs and where degradation is small. Table VI shows all such data obtained in ethane at 150°C in the pressure range of about 20000–25000 psi, and Figure 5 shows these data plotted as logarithm of viscosity versus concentration (i.e., log η versus c).

The averaged data obtained from Table VI and Figure 5 (i.e., least-squared values of η at the various values of c) are retabulated in Table VII and plotted as master plots in Figure 6. All these data can be represented, within limits of 90% confidence, by the equation.

$$\log \eta_r = (0.726 \pm 0.115) + (0.169 \pm 0.011) [\eta]c \qquad (3)$$

where the root-mean square deviation σ is ± 0.140, or by the equation

$$\log \eta_r = (-0.898 \pm 0.259) + (1.083 \pm 0.083) \sqrt{[\eta]c} \qquad (4)$$

where the root-mean square deviation σ is ± 0.164.

By using eq. (3), activation energies from Tables IV and V, ethylene viscosities from Figure 3, and the solvent correction for the relative viscosity from Table III, viscosities for the system LDPE–ethylene can by computed (Table VIII). These computed values should represent the
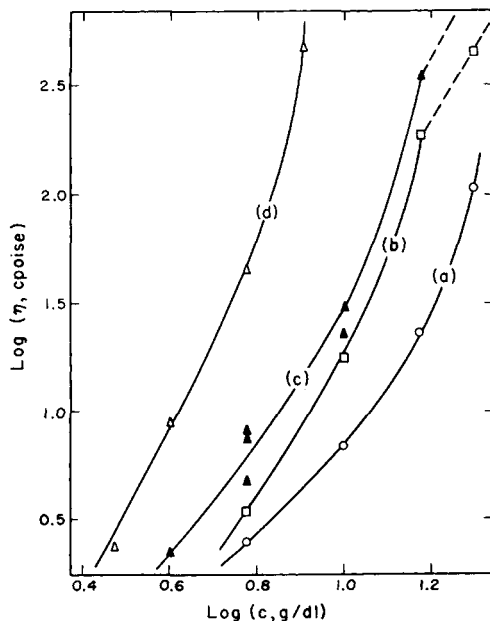

Fig. 5. Logarithm of relative viscosity vs. concentration of LDPE in ethane at 150°C and 20000–25000 psi; (○) LDPE type A; (□) LDPE type B; (△, ▲) LDPE type C.

TABLE VII

Viscosities for Ethane Solutions at 150°C, Averaged Data from Table VI and Figure 5

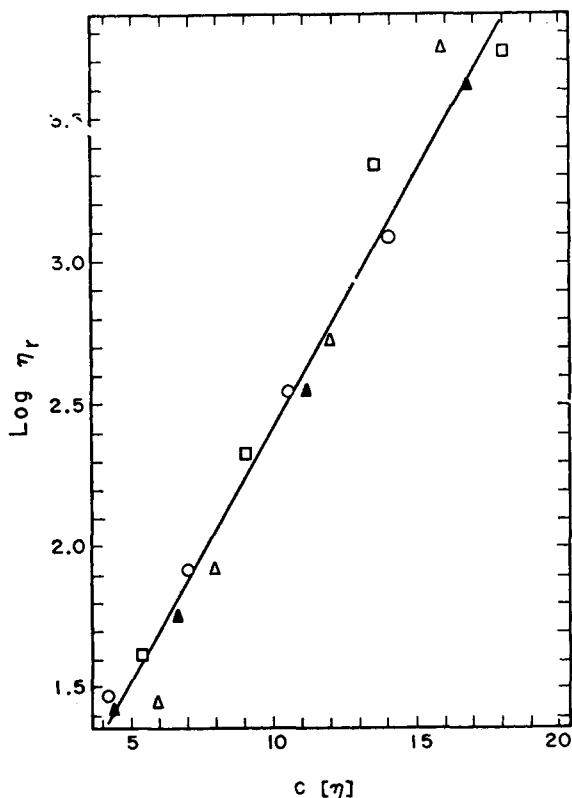| LDPE | Functions | Concn c, g/dl |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| | | 3 | 4 | 6 | 8 | 10 | 15 | 20 |
| Type A | $\log \eta$ | | | 0.395 | | 0.864 | 1.451 | 2.038 |
| | $\log \eta_r$ | | | 1.466 | | 1.935 | 2.522 | 3.109 |
| | $[\eta]c$ | | | 4.20 | | 7.00 | 10.5 | 14.0 |
| Type B | $\log \eta$ | | | 0.601 | | 1.235 | 2.030 | 2.820 |
| | $\log \eta_r$ | | | 1.672 | | 2.306 | 3.099 | 3.891 |
| | $[\eta]c$ | | | 5.40 | | 9.00 | 13.5 | 18.0 |
| Type C | $\log \eta$ | 0.250 | 0.422 | 0.763 | | 1.453 | 2.312 | 3.172 |
| | $\log \eta_r$ | 1.323 | 1.495 | 1.846 | | 2.526 | 3.385 | 4.245 |
| | $[\eta]c$ | 3.33 | 4.44 | 6.66 | | 11.1 | 16.7 | 22.2 |
| Fraction 2 | $\log \eta$ | 0.362 | 0.954 | 1.653 | 2.681 | | | |
| | $\log \eta_r$ | 1.476 | 1.924 | 2.819 | 3.715 | | | |
| | $[\eta]c$ | 5.94 | 7.92 | 11.9 | 15.8 | | | |

Fig. 6. Correlation of relative viscosity η_r of LDPE in ethane at 150°C with concentration c and intrinsic viscosity $[\eta]$ (in p-xylene at 105°C), averaged data from Table VI and Fig. 5 (see Table VII and text): (O) LDPE type A; (□) LDPE type B; (△,▲) LDPE type C.

correct Newtonian viscosities to within a factor of well less than two and should provide a rather accurate estimate of the effects of changes in concentration and molecular weight on the viscosity.

DISCUSSION

As shown by Figure 6 and eq. (3) all the η_r–$[\eta]$–c data in Table VII are represented to a reasonably good approximation by a linear plot of log η_r versus $[\eta]c$. The significance of the dimensionless parameter $[\eta]c$ as the abscissa in the representation of viscosity data was discussed by Weisberg et al.[12]   More commonly, the parameter $[M^{0.68}\,c]^{1/2}$, which is essentially equivalent to $\{[\eta]c\}^{1/2}$, is used as the abscissa in representations of log η_r data.   Such plots approach linearity at large values for the abscissa for some polymer solutions.[13]   As shown by Figure 6 and eq. (4) all our η_r–$[\eta]$–c data in Table VII also can be represented to a reasonably good approximation by a plot of log η_r which is linear in $\{[\eta]c\}^{1/2}$.

TABLE VIII
Viscosities of Ethylene Solutions

LDPE type	Concn c, g/dl	Viscosities		
			Solution η, Cp[b]	
		Relative η_r[a]	At 200°C	At 250°C
A	5	29.1	2.1	1.5
B	5	43.0	3.1	2.3
C	5	64.7	4.6	3.3
A	7.5	57.5	3.9	2.7
B	7.5	103	6.9	4.85
C	7.5	190	13	8.9
A	10	114	7.15	4.8
B	10	247	16	10.4
C	10	561	35	23.5
A	12.5	224	13	8.4
B	12.5	594	35	22
C	12.5	1650	98	62
A	15	444	25	15
B	15	1420	79	48
C	15	4860	270	160
A	20	1730	85	46
B	20	8220	400	220
C	20	42,200	2100	1100

[a] Relative viscosity of LDPE in ethylene at 150°C, calculated on the basis of eq. (3) and the assumption that at a given temperature η_r for the ethylene solutions is 1.40 η_r for the ethane solutions (see Table III).

[b] Calculated on the basis of the assumptions that (a) the activation energies for η are 0.5, 1.0, 1.5, 2.0, 2.5 and 3.5 kcal/mole for the solution concentrations tabulated, respectively, and (b) that viscosities of ethylene η_0 are 0.076 Cp at 200°C and 0.059 Cp at 250°C.

No physical significance should necessarily be attached to the fact that the data of Table VII can be represented by a plot of log η_r which in linear in $[\eta]c$. This apparent correlation may be entirely the result of experimental error and the limited range of the abscissa over which data were obtained.* It may be worth noting that although use of the parameter $[\eta]c$ appears to be justified by the considerations of Weisberg et al.,[12] eq. (3) is different from the generally useful empirical Baker equation[14] and does not represent the limiting form of the equation $(\eta_r - 1)/c = [\eta] \exp \{k'[\eta]c\}$ which is another reasonably successful empirical representation of viscosity data.[14]

It should be noted that the activation energy obtained in this study is a constant volume activation energy. Ordinarily the quantity measured is a constant pressure activation energy. In undiluted systems, the relation between the two is determined by the flexibility of the polymer molecule and by the internal pressure of the polymer.[15]

* The latter point was emphasized to us by Dr. R. F. Landel.

The nature of eq. (3) is such that, for polymer of relatively low viscosity-average molecular weight at relatively low concentration, the absolute solution viscosity may seem surprisingly low. This behavior is certainly partly a result of the low solvent viscosity. However, it is also possible that, in the terminology of F. Bueche,[16] the polymer chain may be characterized by an abnormally high jump frequency and hence an abnormally low segmental friction factor when compared to solutions studied under more familiar conditions.

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