High-Pressure Viscosity and Density of Polyethylene Solutions in *n*-Pentane

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SYNOPSIS

Viscosity and density of homogeneous one-phase solutions (1 wt %) of polyethylenes with narrow molecular weight distributions (M_w = 2150, 15,520, 108,000, and 420,000) in *n*-pentane were determined at 398, 413, and 428 K over a pressure range from 20 to 60 MPa. Measurements were done with a special falling cylinder type viscometer that permits simultaneous determination of viscosity, density, and phase state of the solutions. It is shown that the viscosities of these solutions can be correlated with density (ρ) using the exponential relationships $\mu = A \exp \{B/(1 - V_o\rho)\}$ or $\mu = C_1 \exp (C_2\rho)$, which are based on free-volume considerations. Analysis of the temperature dependence of viscosity at fixed pressures, and its pressure dependence at fixed temperatures show that the flow-activation energies for these solutions are in the range 8–12 kJ/mol, and the apparent activation volumes are in the range 30–45 cm^3/mol. Evaluation of the specific viscosity and analysis of the molecular weight dependence of intrinsic viscosity in accordance with Mark–Houwink type relationship $\mu = \mathrm{KM}^a$ suggest a value of 0.5 for the exponent a, which is typical of poor or theta solvents.

INTRODUCTION

Information on high-pressure viscosity of polymer solutions is of special importance in applications related to natural processes,[1] high-pressure lubrication,[2,3] enhanced oil recovery,[4,5] and, more recently, to processing of polymers using near- and supercritical fluids.[6-15] As discussed in recent review articles,[10a,b] supercritical fluids are, indeed, being explored as process solvents or as processing aids in a variety of polymer related applications. These include polymerizations, polymer modifications (such as lowering the glass transition temperature for impregnations with additives or dyes), polymer processing schemes (such as lowering the viscosity of molten polymers in extruders), and composites manufacturing by impregnations of microporous substrates such as wood or fibrous mats with polymers or their precursors.

In addition to utilization in such practical applications, there is theoretical interest in investigation of viscosity of polymer solutions at high-pressures especially in near- and supercritical fluids in which the "goodness" of the solvent, that is, the solvent power, can be changed by manipulation of the fluid pressure or density.[6,7,16-21] The measurement of viscosity as a function pressure or density, in particular, evaluation of the intrinsic viscosity, can provide valuable information on the changes in the solvent–polymer interactions and the hydrodynamic volume of polymer as the system conditions are changed.

Viscosity data for polymer solutions in near- or supercritical solvents appear to be first reported for solutions of polystyrene in *n*-butane and *n*-pentane,[6-8] and have been recently expanded to other polymers such as polyethylene,[11] polydimethylsiloxane,[12,13,15] and polyisobutylene.[14] Table I is a comprehensive summary of the available literature on the high-pressure viscosity of polymer/solvent systems. Data is rather limited, with essentially no publications prior to 1979. Majority of the data, even though for some systems cover extreme pressures (up to 20,000 bar) are at relatively low temperatures.

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Table I Literature on High Pressure Viscosity of Polymer Solutions

Polymer/Solvent	Temperature Range K	Max Pressure MPa	Reference
PS/trans-decalin	293–318	40	Kubota and Ogino (1979)[16]
PDMS/cyclohexylbromide	293–318	40	Kubota and Ogino (1979)[17]
PS/trans-decahydro naphthalene	283–298	100	Wolf and Jend (1979)[22]
PS/*t*-butylacetate	248–293	100	Schmidt and Wolf (1979; 1982)[18,23]
PS/cyclohexane; diethylmalonate	275–305	100	Wolf and Geerissen (1981)[24]
PS/cyclopentane; cyclohexane	293–325	100	Geerissen, Schmidt, and Wolf (1982)[25]
PS/toluene	298–318	100	Claesson, Mcatee, and Ali (1983)[19]
PDMA/isooctane	298–373	350	Schott, Will, and Wolf (1988)[20]
PBMA/2-propanol	313–345	200	Geerissen *et al.* (1991)[26]
PS/*n*-butane;/*n*-pentane	398–443	70	Sen and Kiran (1991; 1992)[6–8]
PS/chloroform	295	2000	Cook, King, and Peiffer (1992)[21]
PIB/THF	295	2000	Cook, King, and Peiffer (1992)[21]
PS copolymer/THF	295	2000	Cook, King, and Peiffer (1992)[27]
PS/*n*-alkane	298–443	70	Khadilkar and Kiran (1993)[9]
PE/*n*-pentane	398–428	70	Gokmenoglu and Kiran (1993)[11]
PDMS/carbon dioxide	303–343	70	Mertch and Wolf (1994)[13]
PIB/ethylene	303–343	50	Mertch and Wolf (1994)[14]
PDMS/carbon dioxide	323–353	10	Gulari and Manke (1994)[12]
PDMS/carbon dioxide	380–420	70	Xiong and Kiran (1994)[15]

PS = polystyrene; PDMA = poly(dexyl methacrylate); PBMA = poly(butyl methacrylate); PIB = polyisobutylene; PE = polyethylene; PDMS = polydimethylsiloxane.

the highest temperature reported represent the data from our laboratory.

In our laboratory, we are especially interested in the viscosity of polymer solutions where the solvent fluid is normally not a solvent for the polymer under ordinary temperature and pressure conditions. For such solutions, if in the course of pressure or temperature changes during viscosity measurements regions of immiscibility are not to be entered, it is important to know where the phase boundaries are located. Depending upon the polymer and the solvent involved, different trends may be observed.[10] At a constant pressure, changing the temperature may result in either complete miscibility, or lead to demixing. For example, at a given pressure solutions of polyethylene in *n*-pentane undergo phase separation upon an increase in temperature, whereas the reverse is observed for solutions of polystyrene in *n*-pentane.[10] We, therefore, use a specially designed viscometer that permits the assessment of the phase-state during the measurements.[6–11,28,29] The effectiveness of this viscometer has already been demonstrated in our earlier work on the high-pressure viscosity of relatively low molecular weight ($M < 10{,}000$) polystyrenes in *n*-alkanes.[6–9] We have recently been investigating the viscosity of solutions of high molecular weight polymers such as polydimethylsiloxanes (in the molecular weight range from about $M_w = 38{,}000$ to 400,000) in supercritical carbon dioxide[15] and polyethylenes in *n*-alkanes.[11] In this article we report on the viscosity of polyethylene standards with molecular weights in the range from 2150 to 420,000 in *n*-pentane.

EXPERIMENTAL

Materials

The polyethylene molecular weight standards with narrow molecular weight distributions were obtained from Scientific Polymer Products. The molecular weights of the samples as reported by Scientific Polymer Products were M_w = 2150, 15,520, 108,000, and 420,000, with the corresponding polydispersities of 1.18, 1.08, 1.32, and 2.66. *n*-Pentane with 99.9% purity was obtained from Aldrich.

Viscometer

Figure 1 is a schematic diagram of the high-pressure high-temperature viscometer. The system permits determination of viscosities, phase behavior, and densities at pressures up to 70 MPa and temperatures up to 200°C.

The design details and operational procedures have been described in our earlier publications.[6-8,28,29] Briefly, the system consists of a view cell (VC) with a fall tube (FT) and a variable-volume part (VVP), all enclosed in a heated oven. The fall-tube assembly mounted on top of the view cell has an internal diameter of 0.794 cm and a fall length of 15 cm. A cylindrical (0.7781 cm diameter and 2.094 cm in length) sinker made up of an aluminum core (for low density) and SS 416 shell is placed inside the tube. The ratio of the sinker-to-tube diameter, which is 0.9799, is greater than 0.93 required for concentric fall and error-free fall time measurements. Three LVDT (linear variable differential transformer) coils (C1) positioned along the fall tube permits the measurement of the fall time of the cylindrical sinker. Another LVDT coil (C2), permits monitoring the position of the piston in the variable-volume part (and, consequently, the internal volume of the system), which is used to determine the density of the contents at any given temperature and pressure. The viscosity of the solution is related to the fall time (t) of the sinker, and the density of the sinker (ρ_s), and density of the solution (ρ) through the basic relationship

$$\mu = K(\rho_s - \rho)t \tag{1}$$

where K is the instrument calibration constant, which may assume different values for different temperature/pressure conditions, as will be discussed in the section on calibration procedure below.

A specially designed electromagnetic stirrer (MS) assembly consisting of a power supply, a controller, and four electromagnetic coils wound around ferromagnetic rods is used to stir the contents of the viscometer. The ends of the rods are pointed towards a mixing bar in the viscometer. The rotation of the mixing bar is obtained in such a way that one pole of the coils attracts the corresponding pole of the mixing bar while another pole repulses it. This alternates among the four poles at any speed adjustable up to 1200 rpm, controlling the speed of the rotation of the mixing bar. The magnitude of the magnetic flux is adjusted, depending upon the vis-

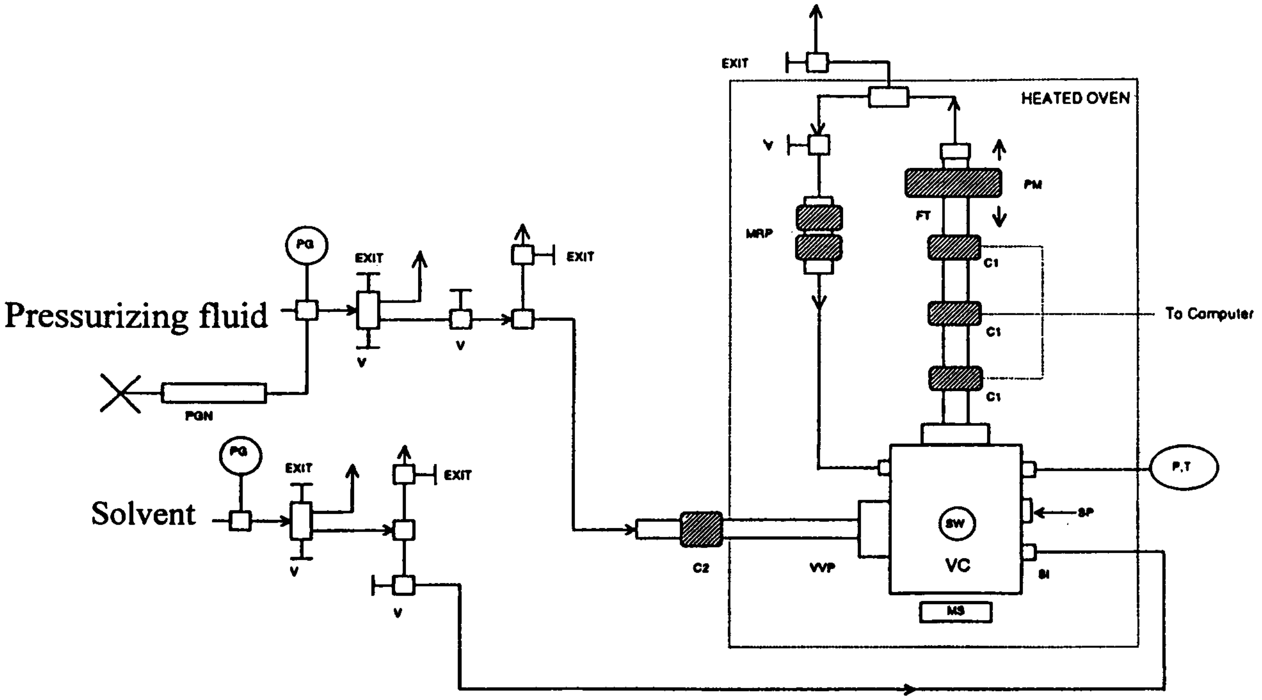

Figure 1 Schematic diagram of the experimental system for measurement of viscosity and density. [VVP = variable-volume piston; VC = view cell; SW = sapphire window; MS = magnetic stirrer; S1 = solvent inlet; SP = solute loading port; P,T = pressure/temperature sensor; FT = fall tube; PM = pull-up magnet; MRP = magnetic recirculation pump; V = valve; C1, C2 = LVDT coils; PGN = pressure generator; PG = pressure gauge].

cosity of the solution and the temperature of the oven. Even though not used for quantitative assessments, the measurement of the magnetic flux to sustain a given rpm, or monitoring the rpm at a fixed magnetic flux as a function of changes in the solution, or the pressure or temperature conditions, may also be viewed as an indicator of the changes in the viscosity of the cell content.

A specially designed magnetic recirculation pump (MRP) provides additional mixing of the whole cell contents to facilitate dissolution and insure homogeneous solutions.

The viscometer temperature is measured with an accuracy of ± 0.5 K and read with a resolution of 0.1 K. Pressures are measured with an accuracy of ± 0.06 MPa and read with a resolution of 0.007 MPa. Fall times are recorded with a computer with an accuracy of ± 2 ms. Volume displacements are determined with ± 0.2% accuracy.

The inlet ports SP and SI are used to load the polymer and the solvent to the viscometer. Once the thermal equilibrium is reached, temperature, pressure, and piston position are all recorded whenever a fall-time measurement is taken. During the fall-time measurements the recirculation pump is stopped. A pull-up electromagnet (PM) is used to reposition the sinker back at the top of the fall tube after each measurement. Sufficient time is given for temperature equilibration before another fall-time measurement is made. Fall-time measurements are conducted at a given temperature over the full range of pressures. The pressure changes are accomplished by changing the position of the piston in the variable volume part of the cell using the pressure generator (PGN).

Calibration Procedure

The goal is to determine the proper value of K in eq. (1) to be used to determine the absolute value of the viscosity at a given temperature and pressure condition. In this particular study, a calibration procedure that is slightly different then previously used[8,28,29] has been employed. The modified procedure[9] starts with the basic assumption that viscosity is a function of $[t\ (\rho_s - \rho)]$ or $[t\Delta\rho]$. For at least four fluids of known viscosity, fall times, t, and the density difference, $\Delta\rho$, are measured at different (at least six) selected temperature and pressure conditions. Then the viscosity of each fluid at each temperature/pressure conditions is plotted as a function of the product $t\ \Delta\rho$. Viscosity of the four different fluids at the same specified temperature/pressure conditions are then fitted into a quadratic equation of the form

$$\mu = A + B[t\Delta\rho] + C[t\Delta\rho]^2 \qquad (2)$$

(This equation is basically of the form of eq. (1) with the correction factor K being a function of $[t\ \Delta\rho]$.) Six such equations are obtained with coefficients A, B, and C corresponding to the six temperature and pressure conditions. These coefficients are summed and averaged to determine a generalized set of coefficients A, B, and C, which are treated as temperature and pressure independent coefficients.

The next stage in the procedure is the incorporation of the temperature and pressure dependence of the calibration constant. This is accomplished as follows. For a selected fluid of known viscosities, at a selected pressure, the fall times (t), and $\Delta\rho$ values are determined at five different temperatures. Using eq. (2) and the average coefficients determined above, viscosities (μ_{est}) are calculated and compared with the literature values (μ_{lit}) at each temperature at the given pressure, and a plot of $[\mu_{\text{est}}/\mu_{\text{lit}}]$ vs. temperature is generated. These plots are fitted into a polynomial of the form

$$[\mu_{\text{est}}/\mu_{\text{lit}}] = a + bT + cT^2 \qquad (3)$$

The procedure is repeated at different pressures and the coefficients a, b, and c are determined at different pressures. The pressure dependence of these coefficients are then tabulated. The next step in the procedure is to calculate the estimated viscosities at a constant temperature (but different pressures) from eq. (2), and generate plots of $[\mu_{\text{est}}/\mu_{\text{lit}}]$ vs. pressure. These are fitted into linear equations of the form

$$[\mu_{\text{est}}/\mu_{\text{lit}}] = \alpha + \beta P \qquad (4)$$

The procedure is repeated this time at different temperatures, to determine the coefficients α and β at different temperatures. Either eq. (3) or eq. (4) can be used to determine the correction factor to be used to convert the estimated viscosity values calculated from eq. (2) to the corrected (true) viscosity values (μ_{corr}) from

$$\mu_{\text{corr}} = \mu_{\text{est}}/C(T,P) \qquad (5)$$

where, $C(T,P)$ is the correction factor that can be evaluated as either

$$C(T,P) = a + bT + cT^2 \qquad (6)$$

or

$$C(T,P) = \alpha + \beta P \qquad (7)$$

in accordance with eqs. (3) or (4).

In the present work, we have used eq. (6) in calculations of the correction factor. Here, the coefficients *a, b,* and *c* are functions of pressure, and their pressure dependence are tabulated as described above. Now the procedure of determining the correction factor at any given temperature and pressure involves determination of *a, b,* and *c* at the specified pressure, and then calculating $C(T,P)$ from eq. (6) at the specified temperature. The real value of viscosity at any T and P, i.e., $\mu(P,T)$ is then given by eq. (5), or more explicitly by

$$\mu(P,T) = \{A + B[t\Delta\rho] + C[t\Delta\rho]^2\}/\{a + bT + cT^2\} \qquad (8)$$

where, t is the fall time measured, $\Delta\rho$ is the density difference between the sinker and the fluid, T is the temperature and A, B, and C are the coefficients independent of temperature or pressure, and the coefficients *a, b,* and *c* are only functions of pressure.

The coefficients A, B, and C were determined using the literature values of the viscosity of *n*-butane, *n*-pentane, hexane, and toluene at T/P conditions of 323 K/53 MPa, 323 K/63 MPa, 373 K/19 MPa, 373 K/33 MPa, 398 K/21 MPa, 398 K/44 MPa.[9] The coefficients *a, b,* and *c* were determined using the literature data for the viscosity of *n*-pentane[30] in the pressure and temperature range of 5 to 70 MPa and 327 K to 444 K. By this procedure, viscosities are determined with an accuracy of ± 3%.[9]

RESULTS AND DISCUSSION

Demixing Pressures

Viscosity measurements were conducted at 1 wt % polymer concentration in the homogeneous one-phase regions. Figure 2 shows the demixing pressures (cloud points) for the polyethylene solutions at 1 wt % concentration. The region above each curve corresponds to the homogeneous one-phase region where the polymer and the solvent are completely miscible.

Phase boundaries for samples of molecular weights 15,520, 108,000, and 420,000 were experimentally determined by procedures described earlier.[31] Briefly, after loading the system with the polymer and the solvent corresponding to a given concentration, temperature and pressure are adjusted until homogeneous one-phase conditions are established. Then, the pressure is slowly reduced by reducing the pressure behind the piston inside the variable-volume attachment of the cell, which is connected to the pressure generation line. After thermal equilibration, demixing pressures are determined by repeated cycling through the phase separation and dissolution point at each temperature. For the 2150 sample, the figure shows the predictions by the Sanchez–Lacombe model.[32] The *P*-*T* envelope for the 1 wt % solution for this low molecular weight polymer sample were not experimentally determined because the temperatures involved are high and approach the upper limit of temperature for the experimental system.

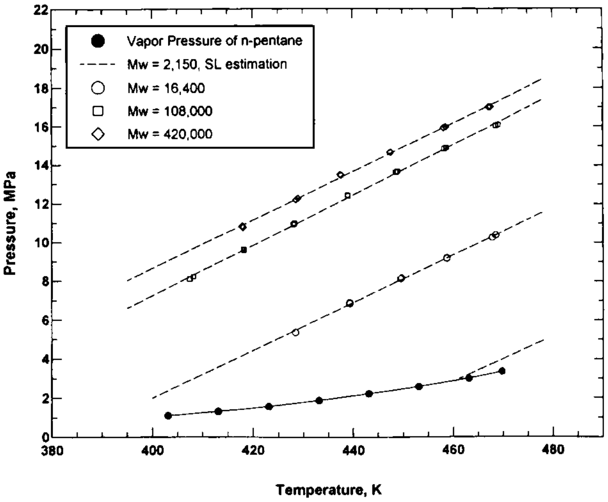

Figure 2 Demixing pressures for polyethylene solutions (1 wt %) in *n*-pentane. Weight average molecular weights are indicated.

As shown in Figure 2, polyethylene–*n*-pentane solutions show the characteristics of systems displaying lower critical solution temperature (LCST). The *P*-*T* curves have a positive slope and at a given pressure, increasing the temperature will cause phase separation.[10,31,32] In the figure, vapor pressure curve for *n*-pentane is also included. This curve ends at the critical point for *n*-pentane (T_c = 469.7 K, and P_c = 3.37 MPa).

The viscosity measurements were conducted at three temperatures (398, 413, and 428 K) in the pressure range from 20–60 MPa, which are much above the demixing pressures. It should be noted that, in the homogeneous regions investigated in the present study, even though pressures are much above the critical pressure of n-pentane, temperatures were below the critical temperature.

Effect of Pressure on Viscosity

Figures 3–6 show the variation of viscosity of the solutions with pressure at the indicated temperatures. As expected, viscosity increases with pressure at a given temperature, and decreases with temperature at a given pressure. Except for the 420,000 molecular weight sample, viscosity of these solutions show a linear variation with pressure. The viscosities change by about 1 to 1.5% per 1 MPa increase in pressure.

The pressure dependence of viscosity for polymer solutions is often discussed in the literature[19,22,25] in terms of the volume of activation in accordance with

$$\mu = A\exp\{(V^{\#}/R\mathrm{T})P\} \tag{9}$$

or

$$\partial \ln\mu/\partial P]_{\mathrm{T,conc}} = V^{\#}/RT \tag{10}$$

where $V^{\#}$ is the volume of activation, R is the gas constant, P is the pressure, T is the temperature, and A is a coefficient.

Figures 7-10 show the ln μ vs. pressure plots for each solution. The activation volume calculated for polyethylene solutions with molecular weights 2150, 15,520, and 108,000 are shown in Table II. (Because of the nonlinear nature of the viscosity-pressure behavior for the 420,000 sample, volume of activation applicable for the full pressure range could not be assigned.) As shown, the volume of activation is in the range from 30–45 cm^3/mol. They are of similar magnitude for the M_w = 2100 and 15,200 but are higher for the 108,000 sample, indicating an increasing effective size for the flow unit. That activation volume increases with the molecular weight of the polymer is documented in the literature for polymer melts. For example, a limiting value (corresponding to very large molecular weights) of 43 cm^3/mol is reported for the activation volume of polydimethylsiloxane melts.[13] For solutions of polydimethylsiloxane in carbon dioxide, depending upon the polymer concentration, activation volumes in the range 11–38 cm^3/mol are reported.[13] For solutions of polystyrene in toluene[19] and cyclohexane[25] activation volumes are about 20 and 36 cm^3/mol, respectively. For these polystyrene solutions, $V^{\#}$ is shown to decrease with temperature, which is interpreted as being due to the greater interaction between the solvent and the polymer with increasing temperature. In contrast, the polyethylene solutions appear to display more of an increase in $V^{\#}$ with temperature. This would be consistent with the fact that these solutions show LCST behavior.

Effect of Temperature on Viscosity

The strong temperature dependence of viscosity for polymer solutions is often described by the exponential Arrhenius type relationships, that is

$$\mu = \mathrm{A}\exp(E/RT) \tag{11}$$

or

$$\ln\mu = \ln A + E/RT \tag{12}$$

where E is the flow activation energy, R is the gas constant, and T is the temperature. Using the data presented in Figures 7–10, ln μ vs. $1/T$, plots have been generated at selected pressures. They are shown in Figures 11–13 for solutions of polyethylene with molecular weights 2150, 15,520, and 108,000. Activation energies that have been calculated are shown in Table III. The activation energies were observed to show a slight increase with molecular weight and are essentially not affected by pressure in the 30–50 MPa range. The activation energies are in the range 8–12 kJ/mol. These relatively low values are not unusual for polymer solutions, especially considering the low polymer concentrations (1 wt %) involved in the present study. For comparisons, it is interesting to note that the high-pressure flow activation energies in the range 5 to 15 kJ/mol are reported for solutions of polydimetylsiloxane in carbon dioxide at polymer concentrations less than 40% by volume.[13] For solutions of polystyrene in cyclopentane (5 wt %), activation energies of about 7 kJ/mol are indicated.[25] For solutions of polystyrene in toluene (0.01 g/mL), flow activation energies are about 6 kJ/mol.[19]

Correlation of Viscosity with Density

Density is known to be an effective scaling factor for viscosity of pure fluids and polymer solutions. Indeed, Enskog equation, or the free volume theories, suggest that viscosity may be expressed as a polynomial or exponential function of density, respectively. In our earlier publications,[6–8,28] we showed that viscosities of n-alkanes, and solutions

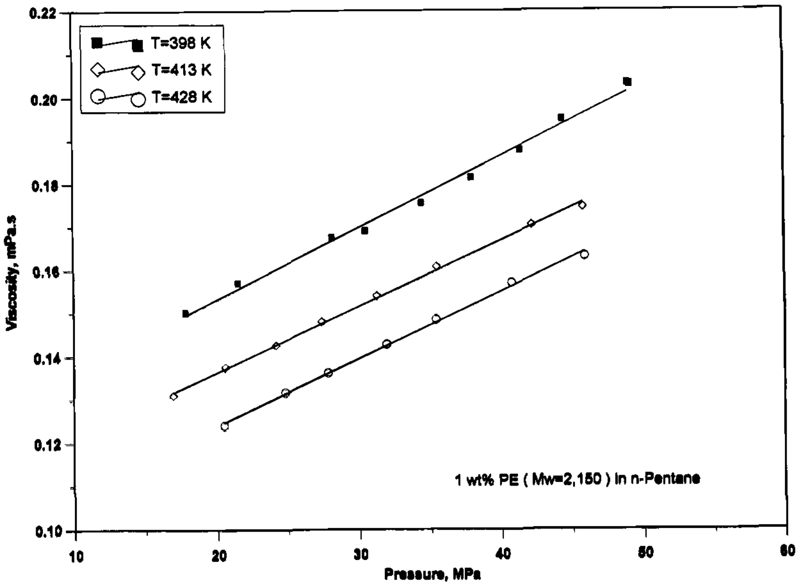

Figure 3 Variation of viscosity with pressure for polyethylene (M_w = 2150) solutions (1 wt %) at different temperatures.

of polystyrenes in *n*-alkanes can be correlated well in terms of density using a functional form of the type

$$\mu = C_1 \exp(C_2\rho) \qquad (13)$$

or

$$\mu = C_3 + C_4 \exp(C_5\rho) \qquad (14)$$

where, C_1, C_2, C_3, C_4, and C_5 are constants.

We have used density scaling and the correlation with these equations in the present study also.

Figures 14–17 show the experimentally determined density values for these solutions as a func-

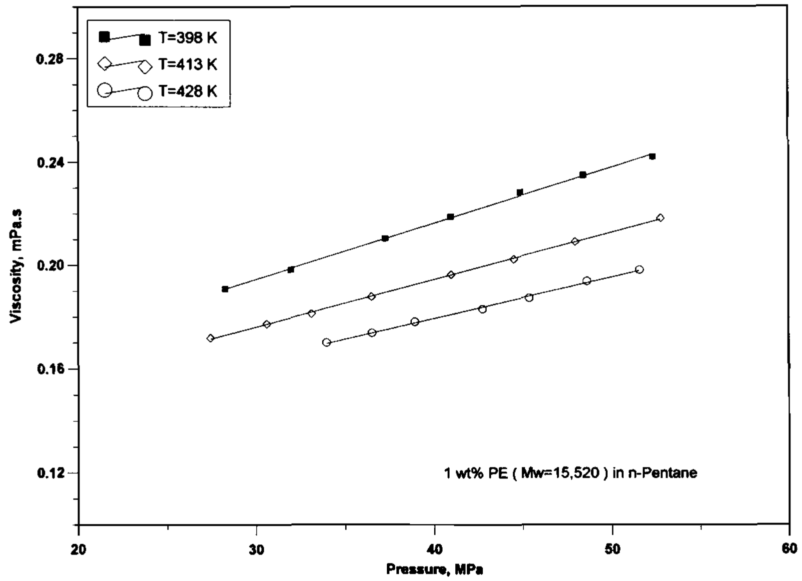

Figure 4 Variation of viscosity with pressure for polyethylene (M_w = 15,520) solutions (1 wt %) at different temperatures.

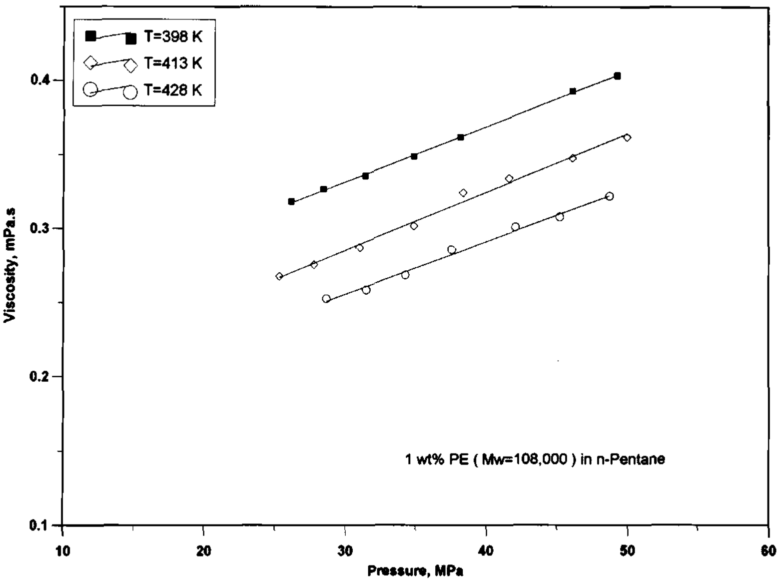

Figure 5 Variation of viscosity with pressure for polyethylene (M_w = 108,000) solutions (1 wt %) at different temperatures.

tion of pressure at the indicated temperatures. Using these density values, viscosity vs. density plots were generated, and eqs. (13) and (14) and other forms based on the free volume theory, especially those conforming to the Doolittle equations, were evaluated.

Figure 18 shows the viscosity vs. density plots for all molecular weights along with the viscosity of the solvent n-pentane. As shown, for each polymer solution, viscosity data corresponding to different temperatures and pressures (see Figs. 3–6) essentially merge into one curve in the density domain. The solid curves in the figures correspond to eq. (13), which led to very good correlations for these solutions. Table IV gives the values of the two parameters for this exponential relationship. Physi-

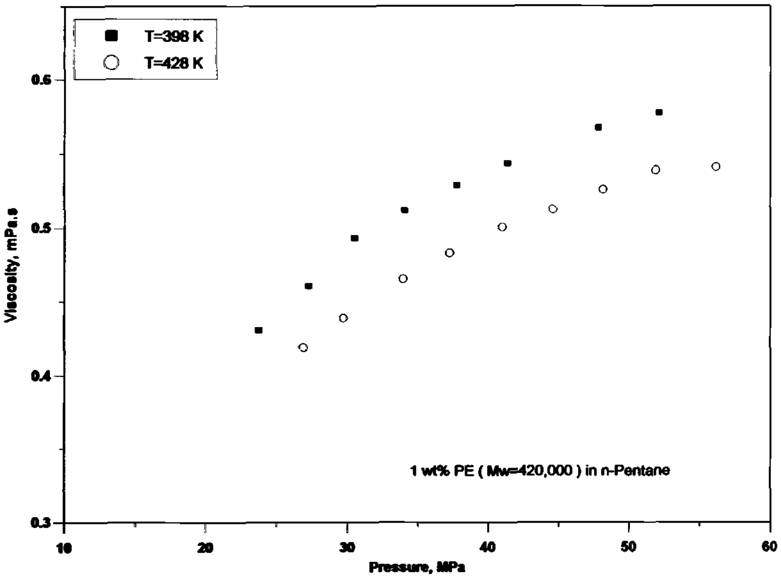

Figure 6 Variation of viscosity with pressure for polyethylene (M_w = 420,000) solutions (1 wt %) at different temperatures.

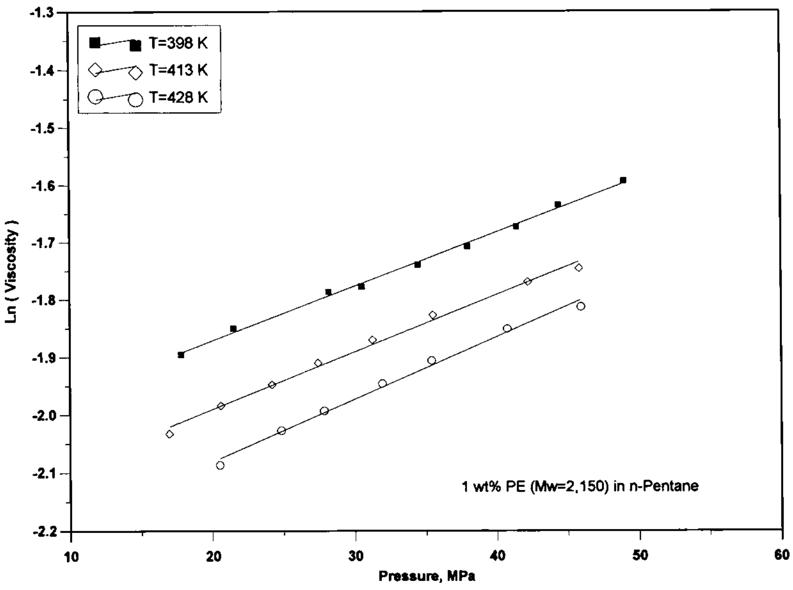

Figure 7 Variation of ln (viscosity) with pressure for polyethylene (M_w = 2150) solutions (1 wt %) at different temperatures.

cally, this simple relationship makes the assumption that the higher the density, the lower is the free volume and, accordingly, the higher is the viscosity. Table IV shows that the C_2 parameter increases with increasing molecular weight. The three parameter relationship given by eq. (14) was not as effective and led to greater errors in estimations, as shown in Table V.

The original Doolittle eqs.[33,34] is given as

$$\mu = \text{A} \exp\{B/(V_f/V_o)\} \tag{15}$$

where V_o is the unit volume extrapolated to absolute zero temperature without change of phase, and V_f is the free volume, that is, $V - V_o$, at the prevailing conditions. Doolittle considered the parameter B to

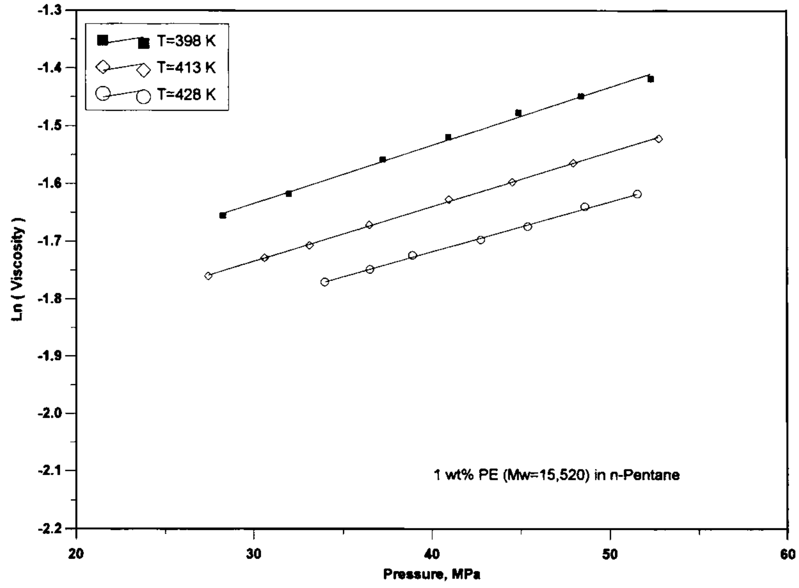

Figure 8 Variation of ln (viscosity) with pressure for polyethylene (M_w = 15,520) solutions (1 wt %) at different temperatures.

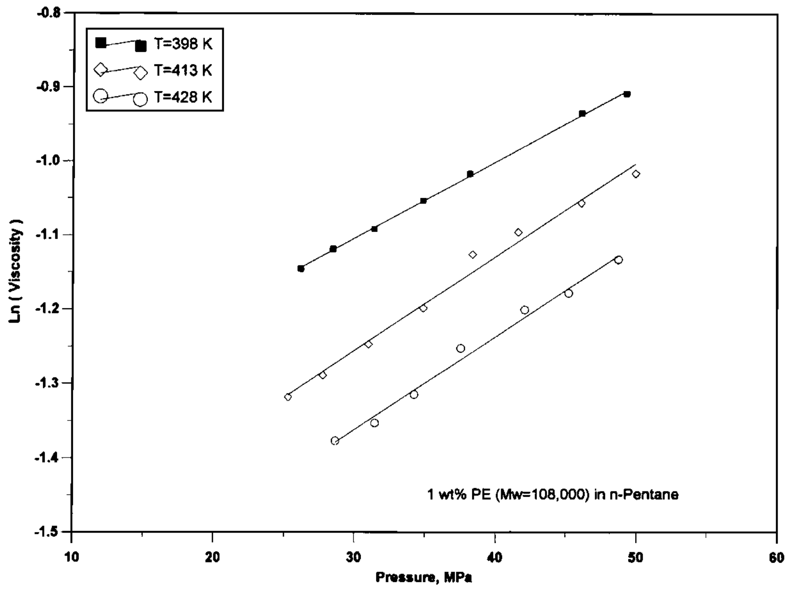

Figure 9 Variation of ln (viscosity) with pressure for polyethylene (M_w = 108,000) solutions (1 wt %) at different temperatures.

be related to the cohesive forces, or the force field intensity resisting flow, and for paraffins, he found the parameter to increase with molecular weight. The parameter A was also found to show an increase with molecular weight for low molecular weight (M_w = 72 to 900) paraffins. Increased separation of molecules and, thus, increased free volume, decreases the viscosity. Other things being equal, changes in the cohesive forces in the solution are linked to the change in free volume, or the extend of separation of molecules from each other.

In terms of the density, eq. (15) can be rewritten as

$$\mu = A \exp\{BV_o\rho/(1 - V_o\rho)\} \qquad (16)$$

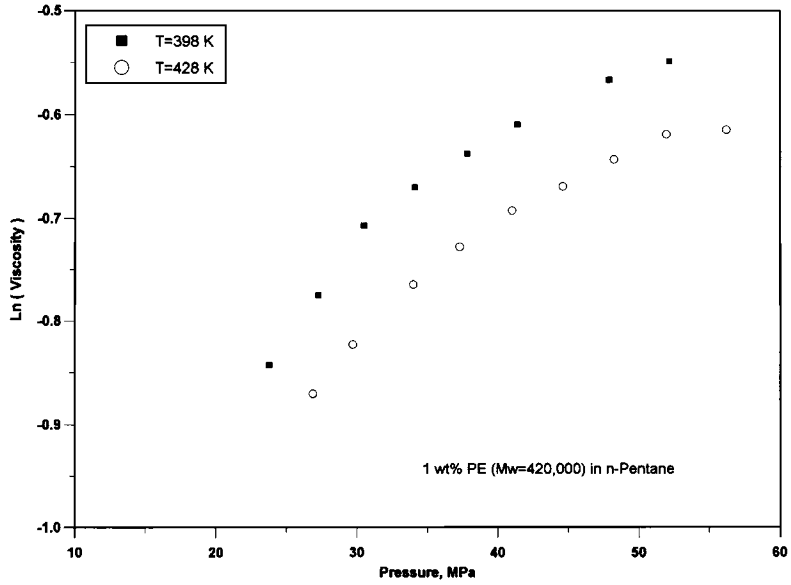

Figure 10 Variation of ln (viscosity) with pressure for polyethylene (M_w = 420,000) solutions (1 wt %) at different temperatures.

Table II Apparent Volumes of Activation ($V^{\#}$) Calculated from $\partial \ln\mu/\partial P]_{T,\mathrm{conc}} = V^{\#}/RT$

	$V^{\#}$		
	Polyethylene solutions with M_w		
Temperature, K	2150	15,520	108,000
398	31.3	33.1	34.2
413	34.1	32.5	43.5
428	38.5	31.0	44.5

or

$$\mu = A \exp\{B^*\rho/(1 - V_o\rho)\} \qquad (17)$$

In this form, the physical meanings of the parameters, as suggested by Doolittle, would be retained, with B^* being equal to BV_o.

We have evaluated the correlative power of eq. (17) also. As shown in Table VI, it gives excellent results. As in the case of paraffins reported by Doolittle, here also the parameters A and B show an increase with the molecular weight of the polymer in the solution. It is interesting to note, however, that the standard errors using these correlations are improved only marginally compared to the errors given in Table IV for the two-parameter correlations, suggesting that the parameter C_2 in eq. (13) essentially mimics the quantity $\{B^*/(1 - V_o\rho)\}$ in eq. (17).

We have evaluated another closely related equation, i.e.,

$$\mu = A \exp\{B/(V_f/V)\} \qquad (18)$$

which in terms of density can be expressed as

$$\mu = A \exp\{B/(1 - V_o\rho)\} \qquad (19)$$

This relationship is similar to the original Doolittle equation, but considers the free volume fraction with respect to the volume V at the prevailing conditions, that is, as $[(V - V_o)/V]$ rather than $[(V - V_o)/V_o]$. The results of these correlations are shown in Table VII. The similarity of the V_o values for all the solutions is not unusual considering the relatively low concentrations that are involved.

Standard errors in estimating the viscosity show that the equations conforming to Doolittle formalism are comparable in their correlation capability. However, the form given by eq. (19) gives V_o values that appear to be more consistent. For these relatively dilute solutions, V_o values should, indeed, be of similar magnitude and be representative of the close-packed volume of the solvent *n*-pentane. (Strictly speaking, V_o is the close-packed volume for the solution, and at higher polymer concentrations should be calculated as a weighted average of the close-packed volumes of the solvent and the

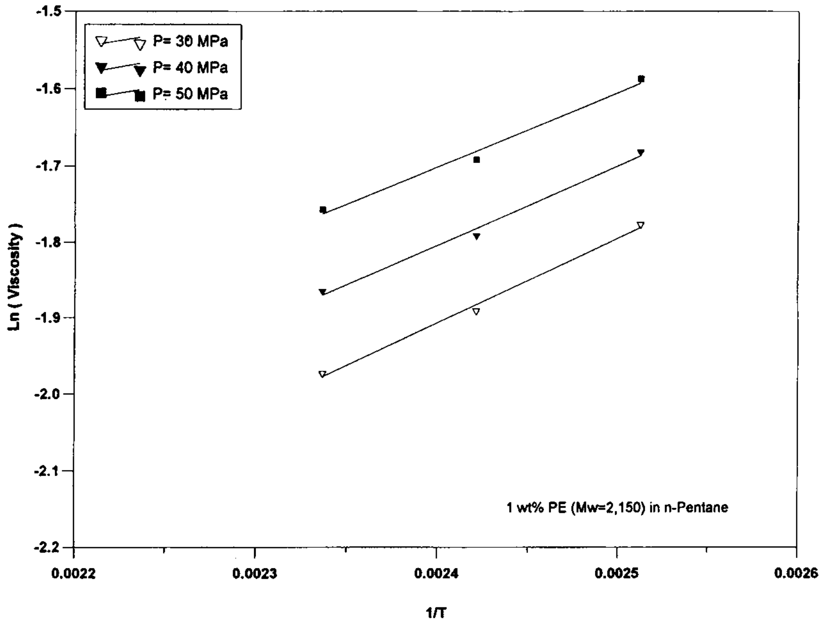

Figure 11 Variation of ln (viscosity) with temperature for polyethylene (M_w = 2150) solutions (1 wt %) at selected pressures.

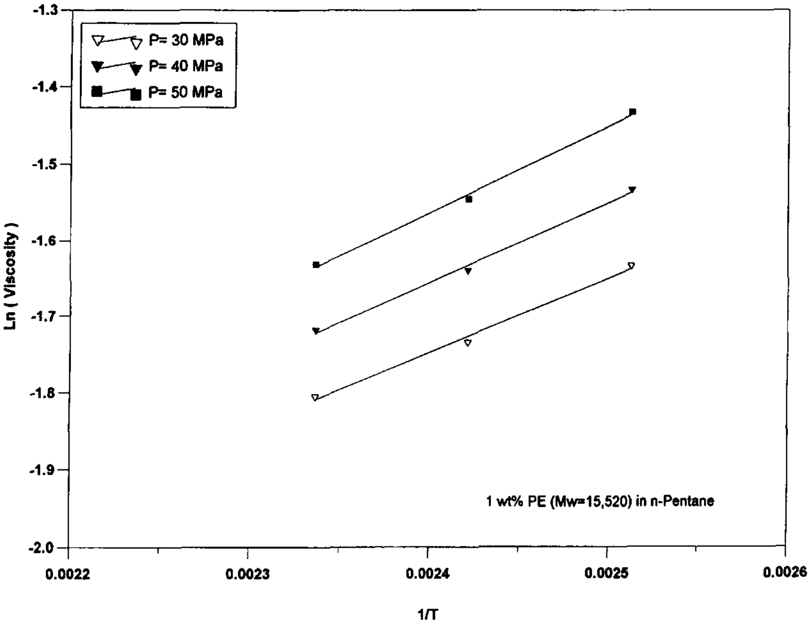

Figure 12 Variation of ln (viscosity) with temperature for polyethylene (M_w = 15,520) solutions (1 wt %) at selected pressures.

polymer.) A value of 0.42 cm^3/g is suggested from the data. A similar analysis with viscosity of carbon dioxide results in a V_o value of about 0.21 cm^3/g.[15] Compared to the close-packed volumes calculated from the cubic equations of state such as van der Waals equation, these are numerically smaller, but remain in similar relative ratios.

Doolittle type relationships have also been found effective by other researchers in describing the effect of pressure on viscosity.[35,36] Values of parameter B

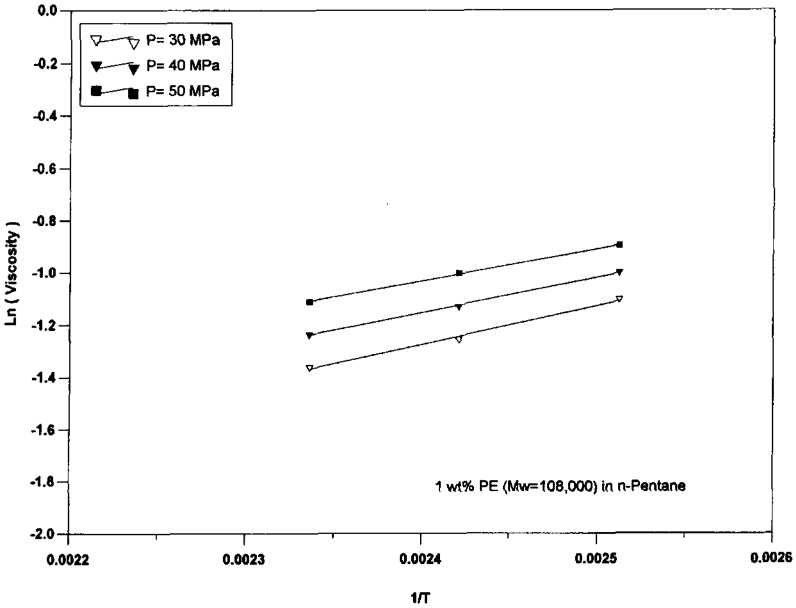

Figure 13 Variation of ln (viscosity) with temperature for polyethylene (M_w = 108,000) solutions (1 wt %) at selected pressures.

Table III **Flow Activation Energies Calculated from $\partial \ln \mu/\partial(1/T)]_{P,\text{conc}} = E/R$**

	E (kJ/mol)		
	Polyethylene solutions with M_w		
Pressure (MPa)	2150	15,520	108,000
30	9.3	8.1	12.2
40	8.6	8.8	11.2
50	8.0	9.4	10.1

has been reported to be in the range from 1 to 10 for various liquids,[35] which are similar to present observations. The parameter V_o is a limiting value that is interpreted as the volume at which viscosity diverges. For liquids, it has been shown to correlate well with the effective hard sphere molecular volume calculated from the modified Carnahan–Starling–van der Waals equation of state.[35]

Effect of Molecular Weight

Figure 18 also provides a comparison of the viscosity of polyethylene solutions of different molecular weight. As expected, viscosity increases with molecular weight of the polymer. Viscosity at these conditions appears to approximately double when molecular weight increases from 15,520 to 108,000, and again appears to double when it increases to 420,000.

Analysis of plots of ln μ vs. ln M at selected constant density conditions (obtained from Fig. 18 and the correlations given in the tables) for this 1% solutions of polyethylene indicates that viscosity behaves approximately as $\mu \sim {M_w}^{0.3}$. It is known that the molecular weight dependence of viscosity for polymer melts or concentrated solutions can be described by either $\mu \sim M$ or $\mu \sim M^{3.4}$, depending upon whether the molecular weight is below or above the critical molecular weight for entanglements.[37] Recent reports on polymer melts show that the critical molecular weight for entanglements is not affected by pressure.[13] Work is presently underway in our laboratory on polymer solutions of different concentrations (higher than 1%) to explore if pressure or density influences the critical molecular weight for entanglements at high pressures.

Specific Viscosity

Specific viscosity values were determined using the defining relationship

$$\mu_{\text{sp}} = [\mu_{\text{soln}} - \mu_{\text{solvent}}]/\mu_{\text{solvent}} \qquad (20)$$

For these calculations, for consistency, viscosity values for the solvent and the solutions were determined from the correlative relationships given by eq. (19) and Table VII. The results are shown in Figure 19. Specific viscosity shows the expected

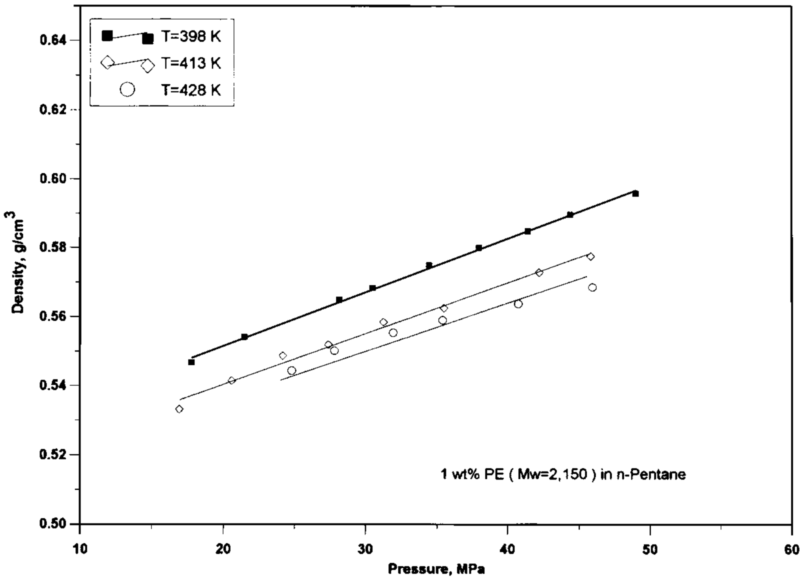

Figure 14 Variation of density with pressure for polyethylene (M_w = 2150) solutions (1 wt %) at different temperatures.

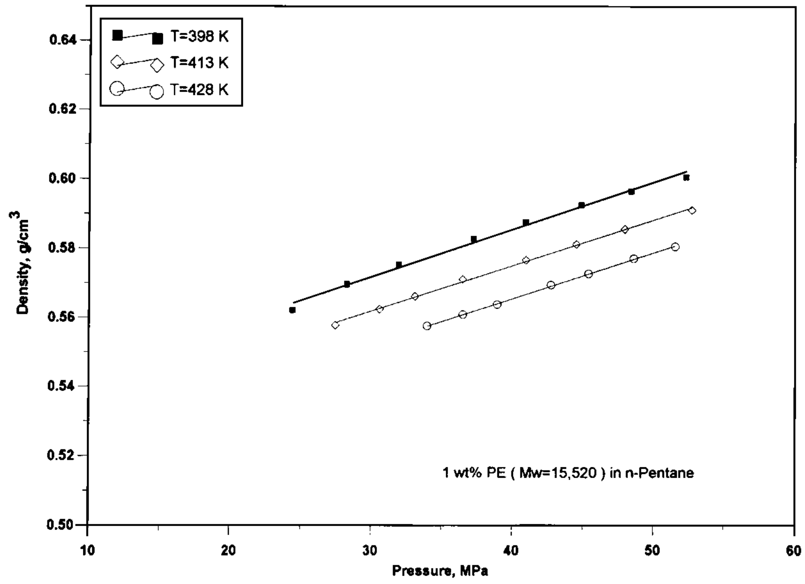

Figure 15 Variation of density with pressure for polyethylene (M_w = 15,520) solutions (1 wt %) at different temperatures.

trends in that it increases with molecular weight and also with increasing density (or decreasing free volume). The increase with density becomes less at higher densities.

Specific viscosity is related to the intrinsic viscosity through

$$\mu_{sp} = [\mu]c + k_H[\mu]^2c^2 \tag{21}$$

or

$$\mu_{sp}/c = [\mu] + k_H[\mu]^2c \tag{22}$$

where $[\mu]$ is the intrinsic viscosity, c is concentration of the polymer (conventionally expressed as g/dL), and k_H is the Huggins interaction parameter. The intrinsic viscosity can be determined from the limit

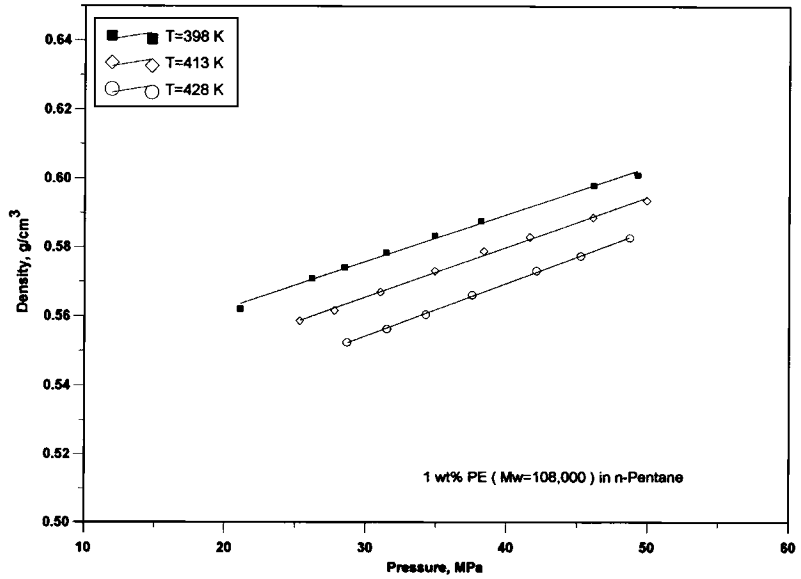

Figure 16 Variation of density with pressure for polyethylene (M_w = 108,000) solutions (1 wt %) at different temperatures.

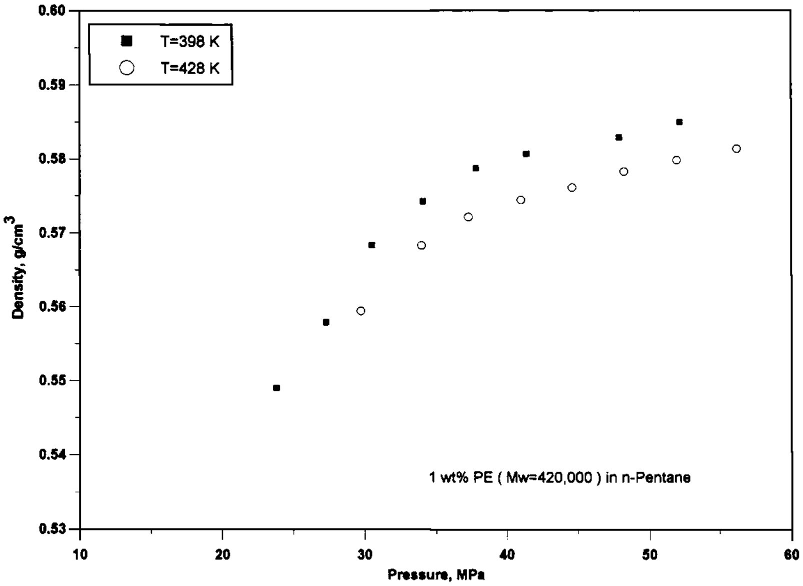

Figure 17 Variation of density with pressure for polyethylene (M_w = 420,000) solutions (1 wt %) at different temperatures.

of μ_{sp}/c as the concentration goes to zero. The significance of intrinsic viscosity is that it is related to the molecular weight, M, of the polymer in terms of the Mark–Houwink relationships according to

$$[\mu] = KM^a \tag{23}$$

or, to the hydrodynamic volume (or the chain coil dimensions) through

$$[\mu]M \sim \; < s^2 >^{3/2} \tag{24}$$

where $<s^2>^{1/2}$ is the radius of gyration.

The exponent a in eq. (23) is intimately related to the polymer–solvent interactions and the goodness of the solvent, and in conventional solvents is typically between 0.5 and 1.0, the value of 0.5 corresponding to the θ conditions.

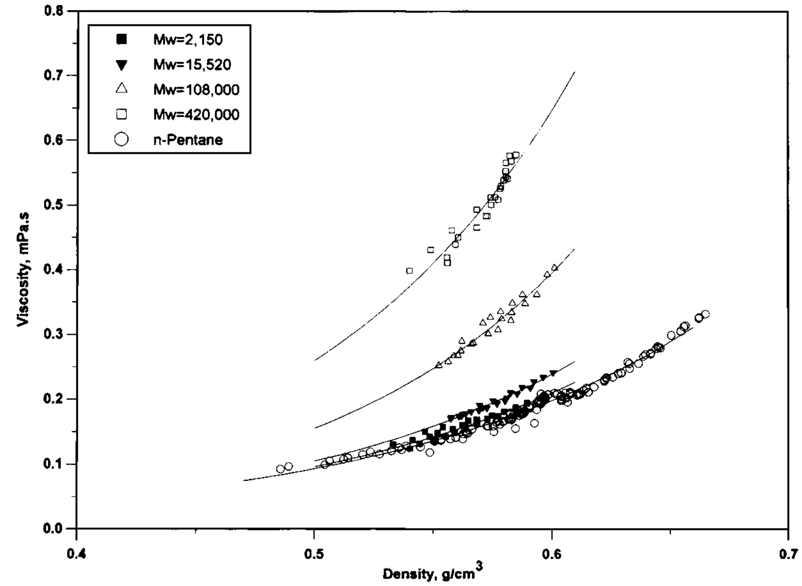

Figure 18 Variation of viscosity with density for *n*-pentane and for polyethylene solutions (1 wt %) in *n*-pentane. Solid lines are correlations.

Table IV Coefficients for the Exponential Equation $\mu = C_1 \exp(C_2\rho)$ for the Density Dependence of Viscosity of Polyethylene Solutions (1 wt %) in *n*-Pentane

Solution	C_1	C_2	SE^a
n-Pentane	0.00214	7.55220	0.010249
2150	0.00193	7.82128	0.006256
15,520	0.00172	8.22204	0.002996
108,000	0.00147	9.32542	0.009202
420,000	0.00273	9.11109	0.015685

[a] Standard error of estimating μ values using the given coefficients. SE = $(\Sigma[y_i - y_{\mathrm{cal}\,i}]^2/n)^{1/2}$, where y_i are the experimental values of a given property, $y_{\mathrm{cal}\,i}$ are the calculated values after regression, and n is the number of data points.

Table VI Coefficients for the Exponential Equation $\mu = A \exp\{B^*\rho/(1 - V_0\rho)\}$ for the Density Dependence of Viscosity of Polyethylene Solutions (1 wt %) in *n*-Pentane

Solution	A	B^*	V_0	SE
n-Pentane	0.0193	2.0230	0.7948	0.009249
2150	0.00554	4.5437	0.4190	0.005256
15,520	0.00567	4.6203	0.4330	0.002937
108,000	0.00648	4.9001	0.4760	0.009218
420,000	0.0108	4.8850	0.4740	0.015442

Recent investigations on the effect of pressure on intrinsic viscosity show that in good solvents, intrinsic viscosity is independent of pressure if the excess volume of mixing is zero.[21] For such systems, the increase in specific viscosity with pressure is interpreted in terms of the increased volume fraction of the polymer per unit volume of solvent.

In near- and supercritical fluid systems, it is known that the solubility and, hence, polymer–solvent interactions may be altered by changes in pressure at a constant temperature or more generally by changes in the density of the solvent (or solution). Determination of the exponent a as a function of density would, therefore, define the θ conditions for such solutions. This condition may be referred to as θ density[6] as opposed to its conventional analogs, the θ temperature at constant pressure, or the θ pressure at constant temperature.

Ideally, intrinsic viscosity should be assessed by extrapolating the reduced viscosity μ_{sp}/c to zero concentration as suggested by eq. (22). Nonetheless, for the present set of data, some of the arguments presented can still be examined using the specific viscosity values at this low concentration to be representative of the intrinsic viscosities at a given density. The increase in specific viscosity with density may be arising either from the solvent becoming a better solvent or from an increase in the volume fraction of the polymer in the solution. From the data presented in Figure 19, we have determined the specific viscosities corresponding to selected densities in the range of 0.55 to 0.65 g/cm^3, and generated plots of ln μ_{sp} vs. ln M (Fig. 20) to estimate the parameters K and a. They are given in Table VIII. Numerical values of K and a are of the same order of magnitude of typical Mark–Houwink constants for polymers in general.[38] It is interesting to note that the a parameter is around 0.5, which would be consistent with the solvent not being a good solvent, but contrary to the initial expectations, does not seem to be affected much by fluid density in this range. It is also interesting to note that despite the fact that viscosities have been determined at conditions far away from the phase separation conditions, the solvent appears to have a numerical value of the characteristic a parameter typical of poor (theta) solvents. The implications of this particular observation, and the general questions regarding density-induced changes in the solvent quality and polymer–solvent interactions are under further exploration in our laboratory.

Table V Coefficients for the Exponential Equation, $\mu = C_3 + C_4 \exp(C_5\rho)$ for the Density Dependence of Viscosity of Polyethylene Solutions (1 wt %) in *n*-Pentane

n-Pentane	−2.89701	1.99867	0.49809	0.017150
2150	−5.22319	4.72207	0.23200	0.005526
15,520	−5.44990	4.78161	0.28900	0.003544
108,000	−6.15304	4.96489	0.46000	0.009463
420,000	−6.63074	5.07683	0.59500	0.017403

Table VII Coefficients for the Exponential Equation $\mu = A \exp\{B/(1 - V_o\rho)\}$ for the Density Dependence of Viscosity of Polyethylene Solutions (1 wt %) in *n*-Pentane

Solution	A	B	V_o	SE
n-Pentane	3.40 E-07	9.90369	0.42317	0.009717
2150	3.10 E-07	9.85144	0.44428	0.005256
15,520	2.92 E-07	9.92685	0.45193	0.002933
108,000	3.22 E-07	9.94026	0.48533	0.009220
420,000	5.35 E-07	9.94361	0.48386	0.015400

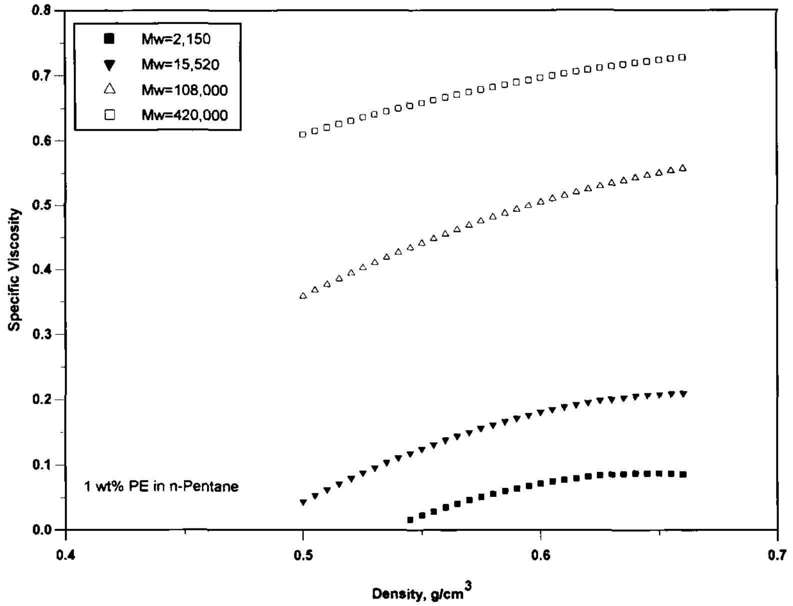

Figure 19 Variation of specific viscosity with density for polyethylene solutions (1 wt %) in *n*-pentane.

CONCLUSIONS

This study has shown that high-pressure viscosity of polyethylene solutions in *n*-pentane can be correlated well with the density of the solutions. Doolittle-type exponential equations based on free volume are shown to describe this dependence better. Temperature dependence is well described by Arrhenius-type exponential relationships. The flow-activation energies are about 10 kJ/mol. Pressure dependence is also correlated with exponential relationships. Apparent volume of activation is in the range 30–45 cm^3/mol. Despite improved miscibility of the polymer with pressure in *n*-pentane in the

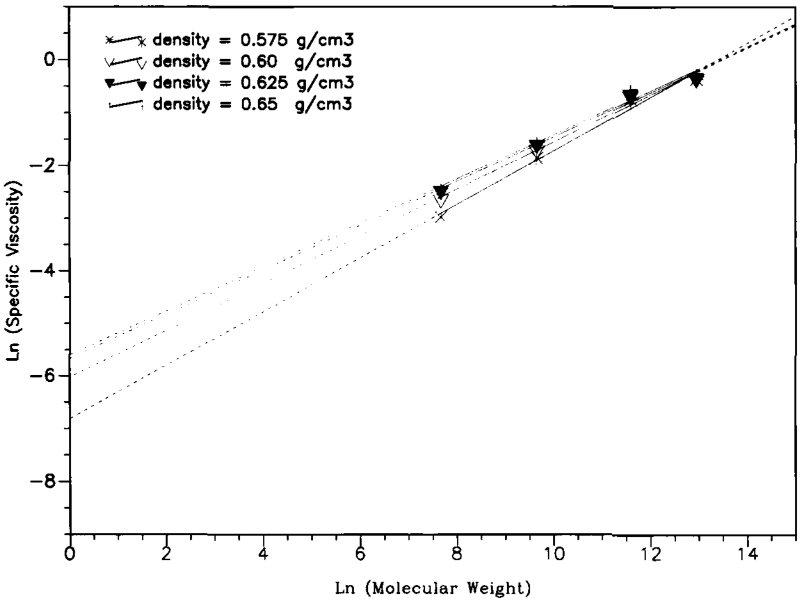

Figure 20 Variation of specific viscosity with molecular weight for polyethylene solutions at selected densities (1 wt %) in *n*-pentane.

Table VIII Mark–Houwink Constants at Different Densities

Density, g/cm^3	ln K	a
0.575	−6.82	0.51
0.600	−6.03	0.45
0.625	−5.66	0.42
0.650	−5.60	0.42

20–60 MPa range, the characteristic behavior of the polymer appears to be similar to that in a poor (theta) solvent.

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