The effect of backbone structure on the cloud point behaviour of polyethylene–ethane and polyethylene–propane mixtures

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Cloud-point data to 155°C and 1300 bar are presented for mixtures of propane and ethane with polyethylene fractionated with respect to molecular weight and degree of chain branching. As the number of chain branches in the backbone of the polyethylene increases, the heat of fusion decreases and the pressure needed to obtain a single phase decreases by ~ 140 bar in ethane and ~ 70 bar in propane. The cloud-point curves for the unfractionated parent polyethylene in either solvent is at higher pressures than those for the fractionated samples, suggesting that high molecular weight oligomers and a broad polydispersity mask the effect of chain structure on the phase behaviour.

INTRODUCTION

The high-pressure phase behaviour of polyethylene (PE)–solvent mixtures is probably one of the most widely investigated polymer systems. Various studies have demonstrated that PE–solvent cloud-point pressures can be decreased substantially if the solvent is a high molecular weight hydrocarbon, and they can be increased substantially if the solvent is either a non-polar or polar low molecular weight hydrocarbon[1-3]. Polyethylene is a non-polar polymer that does not interact favourably with a polar solvent. It has also been demonstrated that the melting point of PE can be depressed substantially as the quality of the solvent increases. The melting point depression is a consequence of the solubility of the solvent in the PE-rich liquid phase.

In this paper we present experimental data that show the effect of backbone structure on the cloud-point behaviour of PE–ethane and PE–propane mixtures. Table 1 lists the physical properties of the six different polyethylene samples used in this study to isolate the effect of molecular weight and molecular weight polydispersity from the effect of structure. The parent sample has a broad molecular weight distribution with a modest weight-average molecular weight. Using a supercritical fluid fractionation technique described by Watkins and coworkers[4], this parent sample was first fractionated with respect to molecular weight. Two samples from the 'fractionated parent', PE_{40A} and PE_{40B}, have much lower polydispersities than the parent material. (The fractionated samples are identified as 'PE_i' where the subscript i designates the percentage crystallinity.) Note that the peak melting temperatures

and the heats of fusion for PE_{40A} and PE_{40B} are reasonably close to that of the parent polyethylene. Watkins et al.[5] further fractionated PE_{40B} to isolate samples with approximately the same molecular weights and low molecular weight polydispersities but with differing backbone structure. Figure 1 shows that PE_{40B} consists of a mixture of 'monodisperse' fractions of varying crystallinity. Table 1 also lists the properties of the three, twice-fractionated samples, PE_{36}, PE_{49}, and PE_{57}, that are used in this study. All three fractions are of similar molecular weight and polydispersity as that of PE_{40B}, although they are much more homogeneous in backbone structure as they were obtained from PE_{40B}.

Table 2 lists the physical properties of the two hydrocarbon solvents, ethane and propane, investigated in this study. Propane has a much higher polarizability than ethane, which indicates that it will be a better solvent for polyethylene. By comparing the phase behaviour of the different polyethylene samples in ethane and propane, the effects of free volume and polarizability

Table 1 Physical property data on the polyethylene samples used in this study

Sample	T_{melt} (°C)	ΔH^{fusion} (J g^{-1})	Percentage crystallinity	M_n	M_w	$\dfrac{M_w}{M_n}$
Parent	123	113	42	21 000	106 000	5.05
PE_{40A}	121	124	46	76 100	108 000	1.42
PE_{40B}	123	108	40	39 300	50 100	1.27
PE_{36}	98	97	36	36 900	49 000^a	1.33
PE_{49}	108	133	49	41 000	53 000	1.29
PE_{57}	123	154	57	37 000	46 000	1.24

^{a} This value is estimated based on the fractionation results reported by Watkins et al.[5]
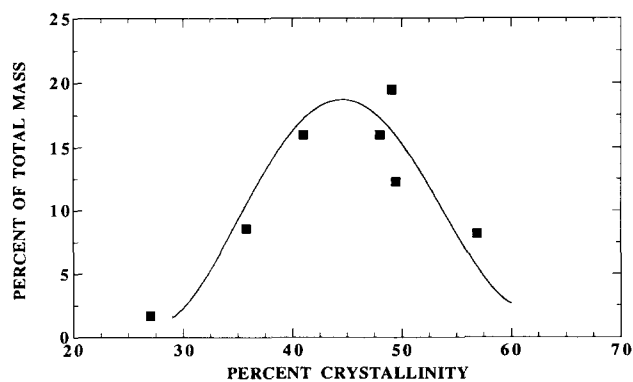
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Figure 1 Percentage crystallinity distribution of the 'fractionated parent' polyethylene. Data of Watkins *et al.*[5]

Table 2 Properties of the solvents used in this study[6,7]. T_c, P_c and ρ_c are the critical temperature, pressure and density, and α is the polarizability

Solvent	T_c (°C)	P_c (bar)	ρ_c (g ml^{-1})	$\alpha \times 10^{25}$ (cm^3)
Ethane	32.3	48.8	0.203	45.0
Propane	96.7	42.5	0.217	62.9

can be determined. Since the polyethylene samples have varying degrees of crystallinity, the solidification boundary will intrude on the fluid-phase portion of the pressure–temperature diagram at temperatures near the melting point of the polymer. The cloud-point curves will be terminated at the crystallization boundary of the polymer. Cloud-point curves are obtained at a fixed concentration of ~ 5.5 wt% polymer which should be reasonably close to the true mixture-critical point[8,9]. In this paper the effect of molecular weight on both ethane and propane will first be presented using fractions PE_{40A} and PE_{40B}. A comparison of these two fractions will enable the determination of molecular weight effects independently of the effect of short-chain branching.

EXPERIMENTAL

Cloud-point curves are obtained using a high-pressure, variable-volume view cell described in detail elsewhere[10,11]. The cell, which has a 1.59 cm i.d., an o.d. of 5.1 cm and a working volume of ~ 22 cm^3, is fitted with a 1.3 cm thick sapphire window to view the phase behaviour and with a moveable piston that is sealed with O-rings to vary the system pressure. A known amount of polymer, to within ± 0.002 g, is loaded into the cell which is then purged at room temperature with the solvent at 3–6 bar to remove any entrapped air. The solvent of interest is then transferred into the cell gravimetrically to within ± 0.002 g using a high-pressure bomb. The pressure of the polymer solution is determined by measuring the pressure (Heise gauge accurate to within ± 2.8 bar) of the fluid behind the piston. A small correction of ~ 1 bar is added to the pressure to account for the pressure needed to move the piston. The temperature of the cell, which is measured to within ± 0.2°C using a platinum-resistance device connected to a digital multimeter, is also maintained to within ± 0.2°C. The contents of the cell are mixed by a stir bar activated by a magnet located below the cell.

The cloud-point pressure is defined as the point at which the mixture becomes so opaque that it is no longer possible to see the stir bar in the solution. The cloud-point curves are repeated at least twice at each temperature, and are reproducible to within ± 5 bar.

RESULTS

Figures 2 and *3* show the cloud-point curves for the six polyethylene samples in propane. *Figure 2* illustrates the effect of molecular weight and polydispersity on the cloud-point behaviour of PE–propane mixtures. Note that the parent PE–propane cloud-point curve is close to the PE_{40A} curve since both polymers have virtually identical weight-average molecular weights although very different polydispersities. Also, both the parent PE and the PE_{40A} cloud-point curves are 40–70 bar higher in pressure compared to the PE_{40B} curve as the weight-average molecular weights of these two polyethylenes are more than twice that of PE_{40B}. Note that the melting point for all three polyethylenes is depressed by approximately the same extent (~ 15°C) since all three samples have essentially the same crystallinities and melting temperatures.

As seen in *Figure 3*, the cloud-point pressures for the three 'monodisperse' fractions, PE_{36}, PE_{49} and PE_{57}, in propane increase with increasing crystallinity or, conversely, with decreasing chain branching. It was
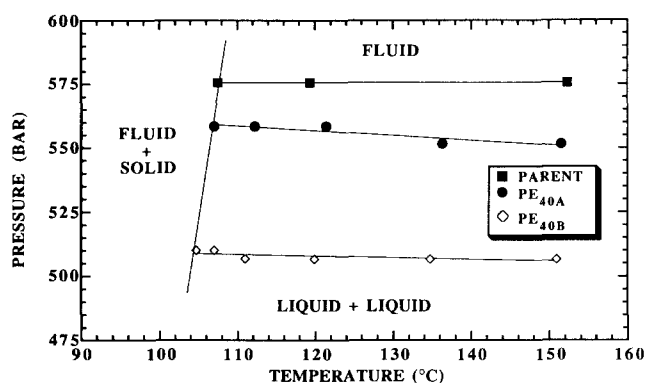

Figure 2 Effect of molecular weight and polydispersity on the cloud-point behaviour of the polyethylene–propane system. The symbols represent experimental data and the lines represent calculations obtained with the Sanchez–Lacombe equation of state
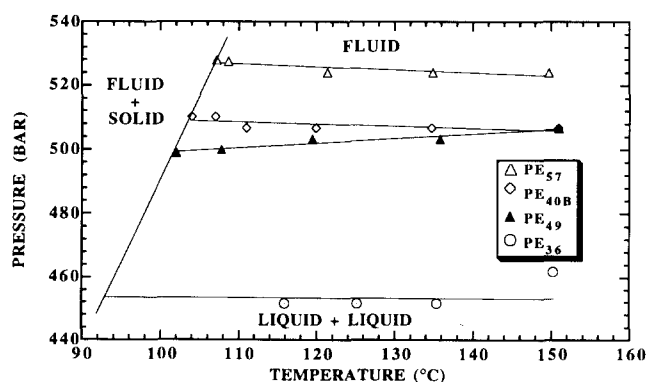

Figure 3 Effect of backbone structure on the cloud-point behaviour of the polyethylene–propane system. The symbols and lines are as in *Figure 2*
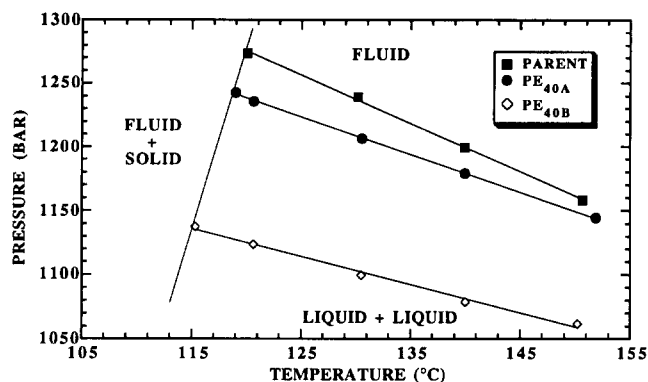
Figure 4 Effect of molecular weight and polydispersity on the cloud-point behaviour of the polyethylene–ethane system. The symbols and lines are as in *Figure 2*

initially surprising that the PE_{40B}–propane system cloud-point curve did not fall below that for the PE_{49}–propane system since the molecular weight and polydispersity are the same as the other three polymers, but the 'weight-average' crystallinity for PE_{40B}, 44% as calculated from the distribution shown in *Figure 1*, is between that of PE_{36} and PE_{49}. Evidently the large amount of high crystallinity polyethylene oligomers in PE_{40B} push the cloud-point curve to higher pressures. The difference in cloud-point pressures between the PE_{57}–propane and the PE_{36}–propane systems is ~ 80 bar, which is similar in magnitude to that caused by differences in polymer molecular weight shown in *Figure 2*. In *Figures 2* and *3* all the cloud-point curves have virtually zero slope, which suggests that if the crystallization boundary did not intrude on the phase boundary the cloud-point curves would eventually exhibit a very steep positive slope with a rapid decrease in pressure with decreasing temperature[2,3].

Figures 4 and *5* show the cloud-point curves for the polyethylene samples in ethane. All the cloud-point curves are at much higher pressures than their counterparts in propane since ethane has a much lower polarizability than propane and therefore it is a much weaker solvent than propane[3]. All the cloud-point curves for the ethane system have very steep negative slopes, which suggests that if the crystallization boundary did not intrude on the phase behaviour the cloud-point curves would have exhibited a rapid increase in pressure with decreasing temperature, a behaviour opposite to that expected for the PE–propane system. *Figure 4* shows that the parent PE–ethane cloud-point curve is close to that of the PE_{40A} system and both curves are ~ 110 bar higher in pressure compared to PE_{40B}, which is a larger difference than that found with the PE–propane system. Note that the melting point depression of the three polyethylene samples in *Figure 4* is less than one half that found with propane.

Figure 5 shows that the cloud-point pressures for the three 'monodisperse' fractions, PE_{36}, PE_{49} and PE_{57}, in ethane follow the same trends as found in propane. The curves increase in pressure with increasing crystallinity or, conversely, with decreasing chain branching. The cloud-point pressures for the PE_{40B}–ethane system are again slightly greater than that of the PE_{49}–ethane system since PE_{40B} has essentially the same molecular weight and polydispersity as the three, twice-fractionated samples, but it has a certain amount of the high-crystalline oligomers. The difference in cloud-point pressures

between the PE_{57}–ethane system and the PE_{36}–ethane system is ~ 140 bar, about twice that found with the propane systems. It is apparent that ethane, the weaker of the two solvents, magnifies the effect of the polymer properties on the phase behaviour. The effect of the polymer properties on the phase behaviour is expected to be further exaggerated by the use of an even poorer solvent such as ethylene.

MODELLING

The Sanchez–Lacombe (SL) equation of state[12] with two mixture parameters is used to model the phase behaviour reported in this study. The objective of these calculations is to determine whether the SL equation is sensitive enough to account for the effect of chain branching. Since PVT data are not available on the various monodisperse, crystalline fractions, the calculations are performed both with low-density and high-density (LDPE and HDPE) pure component parameters to compare the effect of the PE pure component parameters on the calculated cloud-point curves. The SL equation of state is:

$$\tilde{\rho}^2 + \tilde{P} + \tilde{T}\left[\ln(1-\tilde{\rho}) + \left(1 - \frac{1}{r}\right)\tilde{\rho}\right] = 0 \qquad (1)$$

where $\tilde{T}, \tilde{P}, \tilde{v}$ and $\tilde{\rho}$ are the reduced temperature, pressure, volume and density, respectively, that are defined as

$$\tilde{T} = T/T^* \qquad\qquad T^* = \varepsilon^*/R \qquad (2)$$

$$\tilde{P} = P/P^* \qquad\qquad P^* = \varepsilon^*/v^* \qquad (3)$$

$$\tilde{\rho} = \rho/\rho^* = 1/\tilde{v} = V^*/V \qquad V^* = N(rv^*) \qquad (4)$$

$$\rho^* = M/(rv^*) \qquad (5)$$

where T^*, P^* and ρ^*, or equivalently, ε^*, v^* and r, are characteristic parameters for each component in the mixture. *Table 3* lists T^*, P^* and ρ^* for ethane, propane,
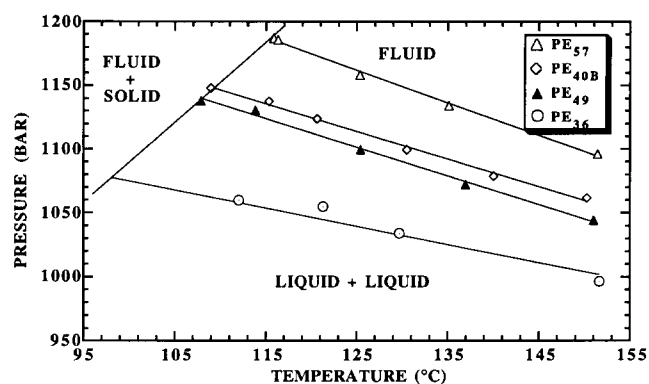

Figure 5 Effect of backbone structure on the cloud-point behaviour of the polyethylene–ethane system. The symbols and lines are as in *Figure 2*

Table 3 Characteristic pure component parameters for the solvents and polymers used with the Sanchez–Lacombe equation of state

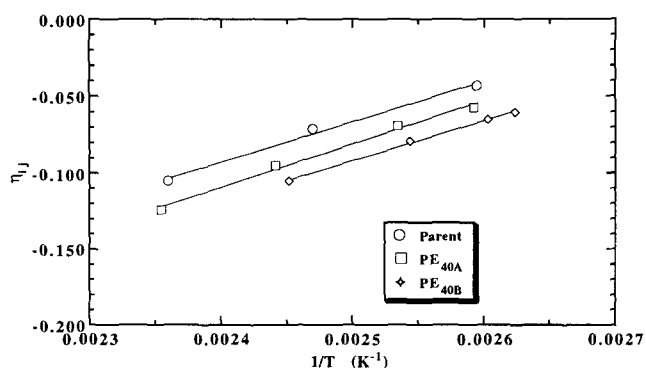| Component	T^* (K)	ρ^* (g ml^{-1})	P^* (bar)
Ethane	315	0.610	3273
Propane	371	0.690	3131
LDPE	671	0.887	3549
HDPE	649	0.904	4250

Figure 6 Temperature dependence of η_{ij} in propane for the three polyethylene samples which differ in polydispersity and molecular weight. For all three polymers, k_{ij} is set equal to -0.020. In this and the next three figures the characteristic parameters of low-density polyethylene were used to fit the cloud-point data

HDPE and LDPE used in the calculations. The characteristic parameters for propane are obtained directly from Sanchez and Lacombe[11] and the parameters for ethane are determined in a manner described previously[3].

The general mixing rules of Sanchez and Lacombe[12,13] are used to calculate the characteristic parameters of the mixture. The mixing rule for the characteristic volume of the mixture, v^*_{mix} is:

$$v^*_{mix} = \sum_{i=1}^{2} \sum_{j=1}^{2} \phi_i \phi_j v^*_{ij} \tag{6}$$

with the cross-term, v^*_{ij}, given as an arithmetic mean of the two pure component characteristic volumes

$$v^*_{ij} = 0.5[(v^*_{ii} + v^*_{jj})](1 - \eta_{ij}) \tag{7}$$

where the volume fractions ϕ_i and ϕ_j, are defined as

$$\phi_i = \frac{m_i}{\rho^*_i v^*_i} \bigg/ \sum_{j=1}^{2} \left(\frac{m_j}{\rho^*_j v^*_j} \right) \tag{8}$$

where m_i is the mass fraction of component i. The parameter η_{ij} accounts for the size differences between segments i and j in the mixture. This parameter is expected to have a large effect on the calculated phase behaviour since it should adjust for the free-volume difference between a segment of polymer and solvent[11].

The mixing rule for the characteristic interaction energy of the mixture, ε^*_{mix}, is

$$\varepsilon^*_{mix} = \frac{1}{v^*_{mix}} \sum_{i=1}^{2} \sum_{j=1}^{2} \phi_i \phi_j \varepsilon^*_{ij} v^*_{ij} \tag{9}$$

with

$$\varepsilon^*_{ij} = (\varepsilon^*_{ii} \varepsilon^*_{jj})^{0.5} (1 - k_{ij}) \tag{10}$$

where k_{ij} accounts for specific interactions between the segments of polymer and solvent. Since polyethylene consists entirely of ethane segments, k_{ij} is set equal to a small number very close to zero because all the i-j interactions should be similar in strength for both the PE–ethane and the PE–propane systems.

The mixing rule for the number of sites a pure polymer molecule occupies, r_{mix}, is given by

$$\frac{1}{r_{mix}} = \sum_{j=1}^{2} \frac{\phi_j}{r_j} \tag{11}$$

where r_j represents the characteristic parameters for component j.

The chemical potential of a component in a mixture, μ_i, is derived as[14]

$$\mu_i = RT \left[\ln \phi_i + \left(1 - \frac{r_i}{r} \right) \right]$$
$$+ r_i \left\{ -\tilde{\rho} \left[\frac{2}{v^*} \left(\sum_{j=1}^{c} \phi_j v^*_{ij} \varepsilon^*_{ij} - \varepsilon^* \sum_{j=1}^{c} \phi_j v^*_{ij} \right) + \varepsilon^* \right] \right.$$
$$+ R T \tilde{v} \left[(1 - \tilde{\rho}) \ln(1 - \tilde{\rho}) + \frac{\tilde{\rho}}{r_i} \ln \tilde{\rho} \right]$$
$$+ P \tilde{v} \left(2 \sum_{j=1}^{c} \phi_j v^*_{ij} - v^* \right) \right\} \tag{12}$$

At equilibrium, the chemical potential of the components present in each of the phases must be equal. If the polymer fractions were truly 'monodisperse' the cloud point would be the intersection of the pressure–composition $(P$-$x)$ isotherm at an overall concentration of 5.5 wt% polymer solution[15–17]. Cloud points are calculated ignoring molecular weight distributions. The pressure–temperature trace of the cloud-point curve is obtained by calculating P-x isotherms at various temperatures. No attempt is made to calculate the pressure–temperature trace of the crystallization boundaries for the two systems studied.

Figures 2 and *3* show the comparison between calculated and experimental cloud-point curves for the PE–propane system. For all the calculations presented with both solvents k_{ij} was set equal to a constant value of -0.020. Also, only the calculated results with LDPE parameters are shown since the results with HDPE parameters are quite similar. A good fit of the experimental data in *Figures 2* and *3* is obtained if η_{ij} is allowed to vary with temperature as shown in *Figures 6* and *7*. All the η_{ij} curves decrease with increasing temperature, reflecting the increased disparity in free volumes between propane and PE with increasing temperature. At high temperatures the close-packed, molar volume of the i-j pair, v^*_{ij}, becomes larger (see equation (7)) due to poor packing of an expanded propane segment with a less-expanded PE segment. Note that the η_{ij} curves are parallel and that η_{ij} becomes more negative with decreasing PE crystallinity, again reflecting the poor packing of an amorphous, branched PE segment with a propane segment.

Figures 4 and *5* show the comparison between calculated and experimental cloud-point curves for the PE–ethane system. A good fit of the experimental data
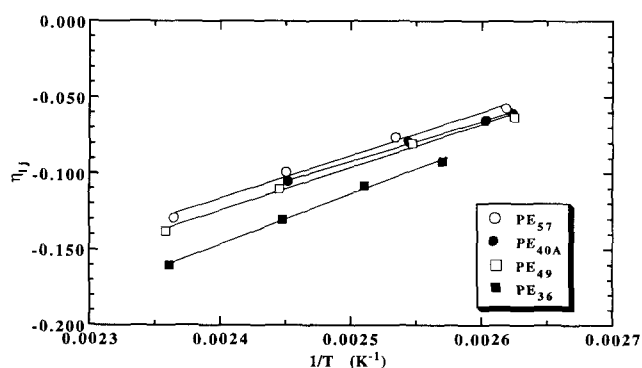

Figure 7 Temperature dependence of η_{ij} in propane for the four polyethylene samples which differ in degree of crystallinity. For all four polymers, k_{ij} is set equal to -0.020
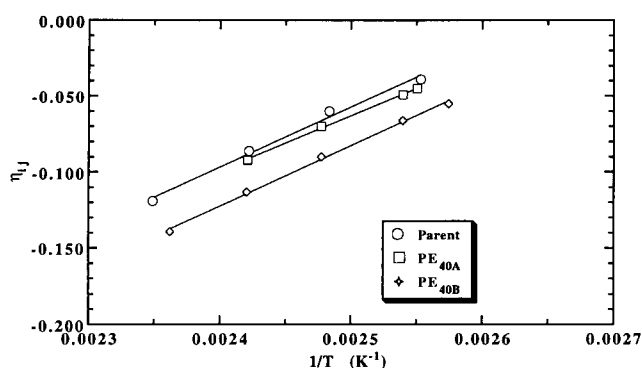
Figure 8 Temperature dependence of η_{ij} in ethane for the three polyethylene samples which differ in polydispersity and molecular weight. For all three polymers, k_{ij} is set equal to -0.020
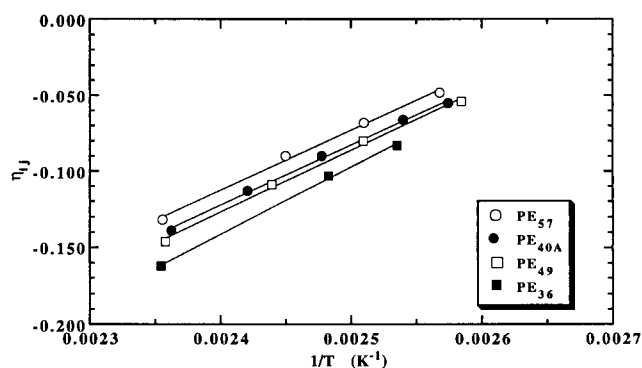

Figure 9 Temperature dependence of η_{ij} in ethane for the four polyethylene samples which differ in degree of crystallinity. For all four polymers, k_{ij} is set equal to -0.020

for the ethane system is obtained if η_{ij} is allowed to vary with temperature as shown in *Figures 8* and *9*. The trends in the η_{ij} curves for the ethane system are similar to those found with the propane system.

The results from the calculations presented here suggest that the variation in the absolute value of η_{ij} may be a consequence of the different backbone structure of the PE polymers. However, the variation of η_{ij} with temperature is more than likely a result of the inability of the SL equation to adequately account for the difference in free volumes between unlike segments as the temperature is varied.

CONCLUSIONS

In this paper we have shown that the backbone structure of polyethylene can have a substantial effect on the location of the cloud-point curve. When comparing the cloud-point behaviour of two different polyethylene samples the effect of backbone structure will be exacerbated if the samples have similar molecular weights and molecular weight distributions. The lower the quality of the solvent, the more pronounced the effect of polymer properties on the phase behaviour. It is possible to model the effect of backbone structure with the Sanchez–Lacombe equation of state using a temperature-dependent mixture parameter that accounts for the packing of unlike segments in solution.

ACKNOWLEDGEMENT

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