Prediction of high-pressure phase behaviour in polyethylene/n-pentane/carbon dioxide ternary system with the Sanchez–Lacombe model

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Polyethylene/n-pentane/carbon dioxide ternary systems have been modelled using the Sanchez–Lacombe lattice-fluid model. Phase diagrams have been generated at pressures up to 300 MPa and temperatures up to 460 K. The results show that the system may display two-phase or three-phase equilibrium depending upon the pressure. At a given temperature, the three-phase regions disappear with increasing pressure. Depending upon the pressure, calculations also predict the experimentally observed shifts from lower critical solution temperature to upper critical solution temperature type behaviours, which are illustrated in the ternary diagrams as shifts in the phase boundaries with temperature. It is further shown that for high-molecular-weight polymer samples the ternary calculations can be simplified by assuming that the polymer-lean phase is essentially free of polymer.

(Keywords: polyethylene; ternary phase diagram; modelling)

INTRODUCTION

Thermodynamics, particularly high-pressure phase equilibria, is key to understanding and development of new supercritical-fluid technologies. Solubility and phase-separation data are needed to evaluate and design new processes. In most cases, such information needs to be generated experimentally. However, experimental effort could be reduced significantly if reliable thermodynamic models for correlating and predicting phase equilibrium data were available. With recent research emphasis shifting more and more to binary and multicomponent fluids, the critical temperature or pressure of which can be manipulated by changing the composition of the solvents, the theoretical predictions of phase behaviour in multicomponent systems has become even more important. For polymer–solvent systems, this type of information is particularly useful for applications related to polymer fractionation, polymer purification, polymer formation and processing with supercritical-fluid media[1].

Explorations for predictive procedures is an ongoing process. Simpler forms of equations of state such as the van der Waals type equations of state and other cubic equations of state are not effective in describing fluids at high pressures. The predictions by these equations of state become even poorer for polymer systems, which is basically due to the large difference between the sizes of a polymer and of a solvent molecule.

In order to model pure fluids and mixtures with arbitrary molecular size, Sanchez and Lacombe[2–5] developed a lattice-fluid model on the assumption of complete randomness of distribution of molecules and holes on the lattice. In this theory, the equation of state has a simpler analytical form compared with other similar equations, for example, the Simha–Somcynsky model[6], which even though it belongs to the same type of approach involves more complex equations. The Sanchez–Lacombe model characterizes the pure fluids by three parameters, namely, the characteristic pressure (P^*), temperature (T^*) and density (ρ^*). Generalization of the model to binary and multicomponent mixtures is straightforward by introducing binary interaction parameters δ_{ij}. There are a number of literature reports on the applicability of Sanchez–Lacombe theory to different systems[7–11]. In our previous study[11], we have reported the effectiveness of this theory in modelling the polyethylene/n-pentane binary system and polyethylene/n-pentane/carbon dioxide ternary system if the ternary is treated as a pseudo-binary mixture. The predictions were found to match the experimental data well. Even though reliable predictions were obtained for the ternary system, the assumption that the solvent can be treated as a pseudo-pure solvent may be restrictive. Therefore, in the present paper, the binary assumption is relaxed and more rigorous calculations using the same theory have been carried out to predict the behaviour of the ternary polymer solutions. The results are presented in the form of ternary diagrams as a function of composition, temperature and pressure.

MODEL

Detailed discussions of the Sanchez–Lacombe model for multicomponent systems have been presented in a recent

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review article[5]. Briefly, the basic equation of state for the model is given by:

$$\tilde{\rho}^2+\tilde{P}+\tilde{T}[\ln(1-\tilde{\rho})+(1-1/r)\tilde{\rho}]=0 \tag{1}$$

where $\tilde{P}$, $\tilde{T}$ and $\tilde{\rho}$ are the reduced pressure, temperature and density respectively, and r is the size parameter, which represents the number of lattice sites occupied by a molecule. The reduced parameters for a pure substance are defined as:

$$\tilde{P}\equiv P/P^* \qquad P^*\equiv\varepsilon/\sigma^3 \tag{2}$$

$$\tilde{T}\equiv \tilde{T}/T^* \qquad T^*\equiv P^*v_0/R \tag{3}$$

$$\tilde{\rho}\equiv\rho/\rho^* \qquad \rho^*\equiv M/v^* \tag{4}$$

$$\tilde{v}\equiv v/v^* \qquad \tilde{v}=1/\tilde{\rho} \tag{5}$$

where σ is the closest distance of approach allowed between two mers, ε is the interaction energy per mer, v_0 is the volume of a lattice site, R is the gas constant, v^* is the hard-core molecular volume (rather than the closed-packed volume of a mer, sometimes also represented by this symbol[1-4,9] and M is the molecular weight. Here it should be pointed out that v_0 is not necessarily equal to σ^3, which was required by the theory in its earlier form[1-4]. The size parameter r is related to the equation-of-state parameters by:

$$r=v^*/v_0 \qquad r=P^*v^*/RT^* \tag{6}$$

Thus, a pure component is completely characterized by three equation-of-state parameters P^*, T^* and v^* (or equivalently ρ^*).

For multicomponent mixtures, these parameters are determined from pure-component parameters using the mixing rules described below.

1. The mixing rule for v^* is based on the assumption that the closed-packed molecular volume of each component is conserved. Therefore:

$$\frac{1}{v^*}=\sum_i\frac{\phi_i}{v_i^*} \tag{7}$$

Here, ϕ_i represents the closed-packed volume fraction of the ith component in the mixture at the limit of zero temperature or incompressible state, and its relation to mass fraction is given by:

$$\phi_i=\frac{m_i/\rho_i^*}{\sum_j m_j/\rho_j^*} \tag{8}$$

where m_i is the mass fraction of the component i.

2. The characteristic pressure P^* for the mixture is given by the following equation[5]:

$$P^*=\sum_j\phi_jP_i^*-RT\sum_j\sum_{i<j}\phi_i\phi_j\chi_{ij} \tag{9}$$

where χ_{ij} is the interaction parameter given by:

$$\chi_{ij}=\chi_{ji}=[\varepsilon_{ii}/\sigma_{ii}^3+\varepsilon_{jj}/\sigma_{jj}^3-2\varepsilon_{ij}(\sigma_{ij}/\sigma_{ii}\sigma_{jj})^3]/kT \tag{10}$$

and

$$\chi_{ii}=0 \tag{11}$$

If a corrected geometric mean approximation is invoked for the cross-terms, i.e. if it is assumed that $\varepsilon_{ij}=(\varepsilon_{ii}\varepsilon_{jj})^{1/2}(1-\delta_{ij})$ and $\sigma_{ij}=(\sigma_{ii}\sigma_{jj})^{1/2}$, then:

$$\chi_{ij}=\frac{P_i^*+P_j^*-2(P_i^*P_j^*)^{1/2}(1-\delta_{ij})}{RT} \tag{12}$$

where δ_{ij} is usually a small quantity and corrects for the deviation of the interaction energy from the geometric mean.

3. The characteristic temperature T^* for the mixture is still defined as

$$T^*=P^*v_0/R \tag{13}$$

which has exactly the same form as in the case for a pure component (equation (3)), but with P^* given by equation (9) and v_0 calculated by following the reciprocal rule:

$$\frac{1}{v_0}=\sum_i\phi_i\left(\frac{P_i^*}{RT_i^*}\right) \tag{13a}$$

Applying these combining rules, the Sanchez–Lacombe treatment leads to the following general expression for the chemical potential of the ith component in a multicomponent system:

$$\frac{\mu_i}{RT}=\ln\phi_i+\left(1-\frac{v_i^*}{v^*}\right)+\tilde{\rho}v_i^*\left(\sum_j\phi_j\chi_{ij}-\sum_i\sum_{j<i}\phi_i\phi_j\chi_{ij}\right)$$
$$+r_i\left[\frac{-\tilde{\rho}+\tilde{P}_i\tilde{v}}{\tilde{T}_i}+\left(\tilde{v}(1-\tilde{\rho})\ln(1-\tilde{\rho})+\frac{\tilde{\rho}\ln\tilde{\rho}}{r_i}\right)\right] \tag{14}$$

where $\tilde{T}_i\equiv T/T_i^*$, $\tilde{P}_i\equiv P/P_i^*$ and $r_i\equiv P_i^*v_i^*/RT_i^*$.

DETERMINATION OF PHASE BOUNDARIES

At a given temperature and pressure, the criterion for equilibrium in the coexisting phases is that the chemical potentials of each component should be equal in all the phases:

$$\mu_i'(T,P,\phi_1',\phi_2',\ldots,\phi_m')=\mu_i''(T,P,\phi_1'',\phi_2'',\ldots,\phi_m'')$$
$$=\mu_1'''(T,P,\phi_1''',\phi_2''',\ldots,\phi_m''')=\ldots \tag{15}$$

where $i=1,2,\ldots,m$, m is the number of components in the system, and the primes stand for different phases. The compositions in each phase must also satisfy the constraint that volume fractions sum up to unity:

$$\sum_{i=1}^m\phi_i'=\sum_{i=1}^m\phi_i''=\sum_{i=1}^m\phi_i'''=\ldots=1 \tag{16}$$

Using the relationship for chemical potential expressed by equation (14), the phase diagrams can be generated for a given system with any number of components by solving equations (15) and (16) simultaneously. The calculations are relatively straightforward for binary systems showing only two-phase equilibrium. In the presence of additional coexisting phases, calculations of the phase boundaries become a more daunting problem. Such complications arise more often in multicomponent systems, such as the ternary systems.

In the rigorous treatment of ternary systems, determining the distribution of the components in the various phases is the most time-consuming step, and simplifying assumptions are often invoked to reduce the complexity of the calculations. For proper simplifications, information on the phase behaviour of the binary branches and *a priori* knowledge of the nature of the ternary system become very helpful. For example, in a ternary system containing polymer, assumptions can be made whether or not the polymer would be present in all phases under a given condition.

According to the phase rule, for a ternary system at a specified temperature and pressure displaying two coexisting phases, the degree of freedom would be equal to one, and only one composition in any coexisting phase must be specified to determine all other equilibrium compositions. In the case of three coexisting phases, the degree of freedom is zero, and therefore the compositions in each phase assume unique values.

For phase equilibrium calculations, one approach would be to locate the three-phase region first. Then, the tie lines of the neighbouring two-phase regions can be easily determined because the sides of the triangle for the three-phase region are essentially the initial tie lines for the corresponding two-phase regions and these sides give a good starting point for the two-phase calculations. This is a straightforward approach when *a priori* information about the three-phase region is available. However, without such knowledge, it is extremely difficult to make an appropriate initial guess for the compositions of each one of the three phases. In the case when the numerical search cannot identify a three-phase region, it may not be easy to discern if this is because of difficulties arising from the computational procedure, or because three-phase regions are in fact absent at the given temperature and pressure conditions. The search process and the numerical calculations procedure, for example, may run into difficulties with a poor initial guess for the compositions of the three-phase region. Therefore, in the present study as described below, an alternative approach has been adopted. In this approach, one of the two-phase regions is located before the three-phase calculations are performed.

Initially we assume that the polymer-lean phase consists of only carbon dioxide and n-pentane (without any polymer), and is in equilibrium with the polymer-rich phase consisting of polyethylene, n-pentane and carbon dioxide. First, a value for the concentration (in terms of the volume fraction) of one of the components in the polymer-lean phase, either carbon dioxide or n-pentane, is assumed. (The volume fraction of the other component in this phase is then fixed.) At a given temperature and pressure, the equilibrium compositions in the polymer-rich phase can be found by solving equations (15) and (16), which reduce to the following:

$$\mu_i'(\phi_2', \phi_3') = \mu_i''(\phi_1'', \phi_2'', \phi_3'') \qquad i = 2, 3 \tag{15a}$$

and

$$\begin{aligned} \phi_2' + \phi_3' &= 1 \\ \phi_1'' + \phi_2'' + \phi_3'' &= 1 \end{aligned} \tag{16a}$$

where a single prime represents the polymer-lean phase, double prime the polymer-rich phase, and 1, 2, 3 represent polymer, n-pentane and carbon dioxide, respectively. In this way, the tie line for the two-phase equilibrium is obtained. The calculations are started from the carbon dioxide-rich end on the carbon dioxide/n-pentane branch of the ternary diagram. The carbon dioxide concentration is then increased by known increments and the calculations are repeated until the full range of compositions on the carbon dioxide/n-pentane axis is covered or up to the composition for which no solutions can be found for equations (15) and (16). Failure to find solutions to equations (15) and (16) means that this two-phase region is terminated at this composition and the boundary of another phase region is reached. The new phase region can be either a one-phase or a three-phase region, which could be judged from whether or not the equilibrium compositions of the calculated two phases converge to the same value (which would imply a one-phase region). If a three-phase region is possible, now with the precise initial guess (the last tie line of the two-phase region actually gives the compositions of the two out of three equilibrium phases), the three-phase region can be easily located. With the known compositions of the three coexisting phases, the next two-phase region, which starts from the other side of the triangular boundary of the three-phase region, can be easily determined. Here the density information of each phase is important in all calculations because either the vapour-like or the liquid-like density must be chosen to calculate the chemical potentials of the components in a given phase. Density information also determines the nature of the calculated phase, i.e. whether it is vapour or liquid.

The assumption that the polymer-lean phase does not contain any polymer must be carefully examined since it may not be acceptable for systems in the vicinity of critical polymer concentration. In the case when both the polymer-lean and polymer-rich phases are permitted to have all three components, calculation procedures essentially follow the same principle, except now equation (15) takes the form:

$$\mu_i'(\phi_1', \phi_2', \phi_3') = \mu_i''(\phi_1'', \phi_2'', \phi_3'') \qquad i = 1, 2, 3 \tag{15b}$$

and

$$\begin{aligned} \phi_1' + \phi_2' + \phi_3' &= 1 \\ \phi_1'' + \phi_2'' + \phi_3'' &= 1 \end{aligned} \tag{16b}$$

and calculations become somewhat more complex. We have also conducted this type of calculation, which would be a more rigorous representation of the ternary system. The results of simplified and rigorous calculations are compared.

EXPERIMENTAL DATA AND CHARACTERISTIC PARAMETERS

Experimental data are the same as reported in our previous publications[12,13]. The characteristic parameters for the Sanchez–Lacombe model are as reported earlier[11] and are listed in *Table 1*.

RESULTS AND DISCUSSION

The binary branches of the ternary system were modelled first. The motivation of analysing the binary branches stems from the following considerations.

(i) It is important to show that the Sanchez–Lacombe theory can predict vapour–liquid transition.

(ii) The binary interaction parameters δ_{ij} can be used directly in ternary calculations since there is no other better way to determine such parameters.

(iii) The binary systems can be used as regressive cases of the ternary systems to guess the location of the three-phase region and check the correctness of the ternary calculations.

Table 1 Characteristic parameters from literature

	P^* (MPa)	T^* (K)	ρ^* (g cm^{-3})	Reference
n-Pentane	310.1	441	0.755	2
n-Butane	322.0	403	0.736	2
Carbon dioxide	574.5	305	1.510	7
Polyethylene	359.0	521	0.895	11

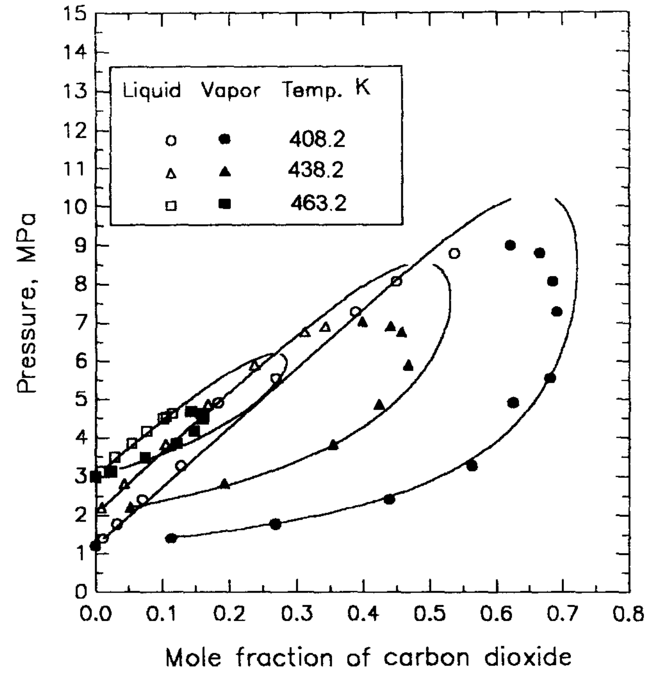

Figure 1 Pressure-equilibrium phase composition diagram for the n-pentane/carbon dioxide binary system. Experimental data are from literature[14]. Full curves are the predictions by Sanchez-Lacombe model. $\delta_{ij}=0.0$ for all calculations

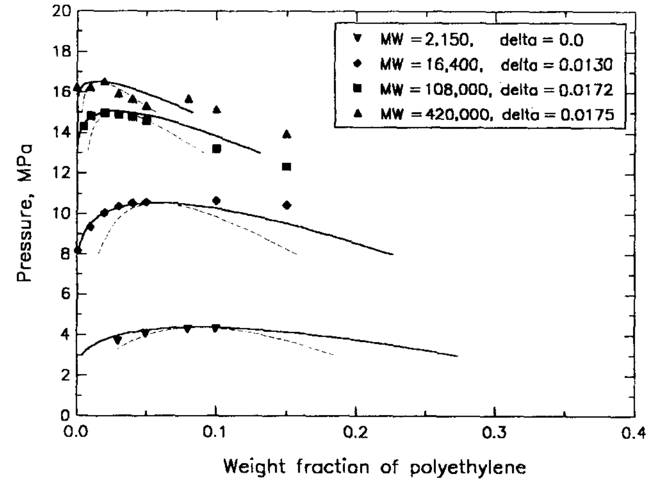

Figure 2 Variation of demixing pressures of PE solutions with polymer concentration and molecular weight at 460 K in n-pentane. Symbols are experimental points. Full curves are calculated binodals, and broken curves are calculated spinodals. Characteristic parameters for polymer: $P^*=359$ MPa, $T^*=521$ K, $\rho^*=0.895\ \mathrm{g\,ml^{-1}}$ (ref. 11)

n-Pentane/carbon dioxide binary system

Figure 1 shows the experimental vapour–liquid equilibrium data[14] at three temperatures for n-pentane/carbon dioxide mixtures. Also shown in the figure are the predictions from the Sanchez–Lacombe model. The interaction parameter used in these calculations is $\delta_{ij}=0.0$. It was optimized to give the least deviation of all the three temperatures over the complete concentration range. The model predicts the pressure range where two-phase behaviour is observed. The predictions are poor near critical points, but become good as pressure is lowered. Similar results have been reported for acetone/propane mixtures using the Sanchez–Lacombe model by Hasch *et al.*[15].

Polyethylene/n-pentane binary system

Detailed calculations for the polyethylene/n-pentane system have already been presented in our previous publication[11]. For the sake of completeness, a summary plot is shown in *Figure 2*. The experimental *P–X* data and the predictions from Sanchez–Lacombe theory are presented for different molecular-weight samples. The full curves are the predicted binodal envelopes and the broken curves are the predicted spinodal envelopes. The characteristic parameters used in the calculations are as shown in *Table 1*. The interaction parameters are indicated in the figure.

Polyethylene/n-pentane/carbon dioxide ternary system

Calculations have been carried out to predict the behaviour of the polyethylene sample with $M_w=108\,000$ ($M_w/M_n=1.32$) in binary solvent mixtures of n-pentane/carbon dioxide. Initially, calculations were carried out by assuming that the polymer-lean phase does not contain any polymer. For the ternary system of polyethylene(1)/n-pentane(2)/carbon dioxide(3), the values of the interaction parameter (δ_{23} and δ_{12}) for the binary branches of carbon dioxide/n-pentane and polyethylene/n-pentane were 0.0 and 0.0172 respectively (see *Figures 1* and *2*). These values, optimized for the binary systems, were used directly for ternary calculations without further adjustments. The interaction parameter δ_{13} for the binary pair polyethylene/carbon dioxide was treated as an adjustable parameter since experimental data for this binary is not available in the literature. The calculations have been performed for the values of δ_{13} ranging from 0.0 to 0.1. The predictions for the phase diagram at 400 K were conducted in the pressure range from 0 to 300 MPa. In *Figure 3*, the results are shown at 50 MPa for different values of interaction parameters. Based on comparisons with the limited experimental data on the phase behaviour (to be discussed later in this section), the appropriate value for δ_{13} was determined to be 0.04 and used in further calculations. Calculations showed that, if pressures are relatively low (<15 MPa), the value of the interaction parameter does not influence the general nature of the phase diagrams and the extents of the phase regions are not much affected. But at higher pressures, the value of the interaction parameter affects the extent of phase

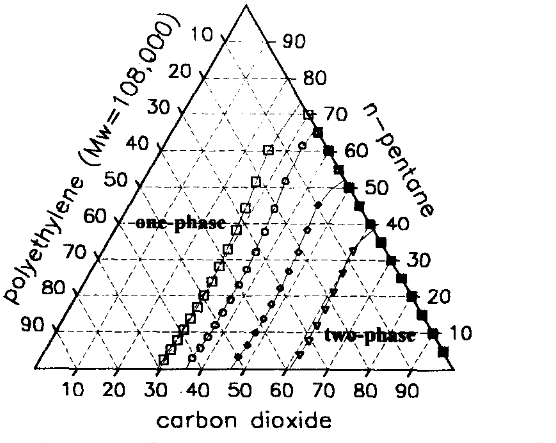

Figure 3 Influence of different values of interaction parameter δ_{ij} for the binary pair polyethylene/carbon dioxide on the predictions of the phase diagrams. Interaction parameters for the binary pairs carbon dioxide/n-pentane and polyethylene/n-pentane are fixed at 0.0 and 0.0172 respectively. Temperature = 400 K, pressure = 50 MPa. δ_{ij}: (□) 0.06; (○) 0.04; (◇) 0.03; (▽) 0.01

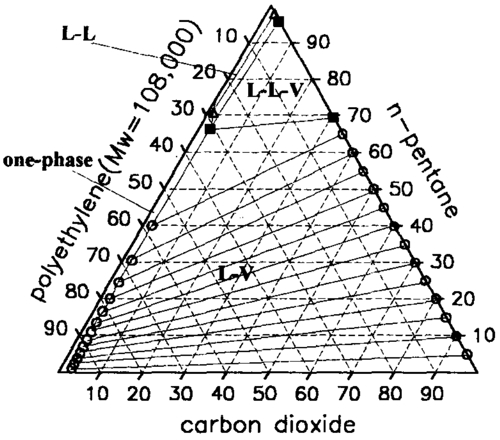

Figure 4 Phase diagram for PE/n-pentane/CO$_2$ system at 400 K and 2 MPa

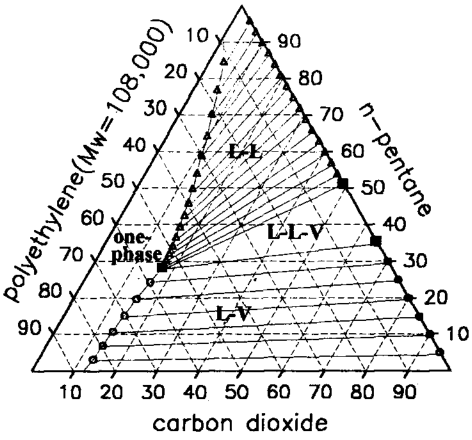

Figure 5 Phase diagram for PE/n-pentane/CO$_2$, system at 400 K and 10 MPa

regions significantly, as illustrated in *Figure 3*. Larger values of δ_{13} were found to lead to a larger area of the two-phase regions and correspondingly smaller area for the one-phase regions.

Figures 4 to *6* show the phase behaviour of polyethylene/n-pentane/carbon dioxide system at 400 K. At relatively low pressures (2 MPa) as shown in *Figure 4*, the dominant feature is the presence of a liquid–liquid–vapour (L–L–V) three-phase region bounded by two two-phase regions (L–V and L–L). The two–phase region (L–V) starting from low pentane concentrations describes the equilibrium between polymer-rich liquid phase and polymer-lean vapour phase. As the n-pentane concentration in the polymer-rich phase increases, the miscibility of the carbon dioxide in that phase also increases and achieves its maximum at the corresponding vertex of the triangular three-phase region (L–L–V). The base of the three-phase region is along the n-pentane/carbon dioxide axis, and the compositions corresponding to the three-phase envelope correspond to the presence of the immiscibility gap in the n-pentane/carbon dioxide binary mixtures, which is in the range from 69.4% to 95.9% n-pentane. This can be further verified from comparisons with *Figure 1* at similar temperature and pressure. The other two-phase region (L–L) at high n-pentane concentrations describes the equilibrium between the polymer-rich liquid phase and polymer-lean liquid phase, but this time with increasing n-pentane concentration in the polymer-rich phase, the miscibility of the carbon dioxide in that phase decreases. As shown in this figure, the one-phase region in which all three components are miscible is very small and confined to carbon dioxide contents of less than 2%.

As shown in *Figure 5*, the general nature of the phase diagram at 10 MPa is similar to the one at 2 MPa. The two-phase region L–V and L–L and the three-phase region L–L–V are observed here also. But the one-phase region is much expanded upon increasing the pressure, indicating that the miscibility of carbon dioxide in polyethylene/n-pentane mixtures is significantly increased.

When the pressure is increased to an even higher value of 25 MPa (as shown in *Figure 6*), the three-phase region disappears and the whole phase diagram simply consists of two regions, namely a two-phase region (L–L) and a one-phase region. The exact pressure where the three-phase region disappears was not determined, but it is expected to be near the critical pressure for the n-pentane/carbon dioxide mixture. The tie lines connect the phases that are polymer-poor and polymer-rich. The remaining one-phase region covers the whole polyethylene/n-pentane axis, which means complete miscibility can be achieved for the ternary mixtures for any concentration of polyethylene as long as the concentration of carbon dioxide is low. When compared with the results at 10 MPa, it is clear that the one-phase region has increased even more at 25 MPa. The one-phase region increases with further increases in pressure. This can be seen from the phase boundaries at 150 and 300 MPa, which are also shown in this figure.

Figures 7 to *9* show the phase behaviour of the system at a higher temperature, at $T=460$ K. At very low pressures (2 MPa, *Figure 7*), the phase diagram is dominated by a large liquid–vapour (L–V) two–phase region. The vapour phase is carbon dioxide and n-pentane, and the liquid phase is the polymer-rich phase. No three-phase region could be identified at this condition, which is in contrast to the observation at 400 K (*Figure 4*) for the same pressure. As can be seen in *Figure 1*, complete miscibility of n-pentane and carbon dioxide over the whole composition range can be achieved either at a very low pressure, which leads to homogeneous vapour phase, or at high pressure, which leads to homogeneous dense fluid phase. The vapour–liquid

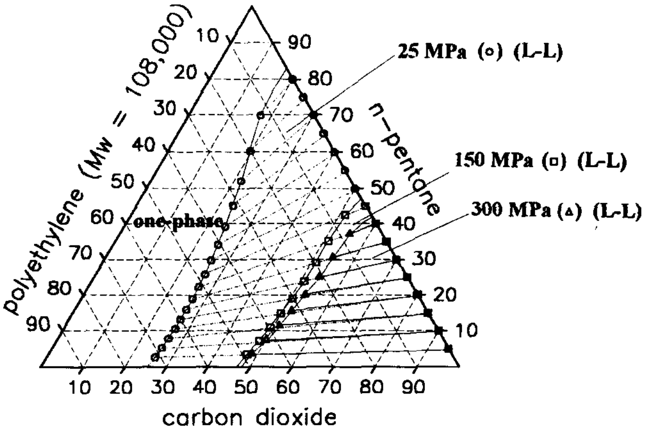

Figure 6 Phase diagrams for PE/n-pentane/CO$_2$ system at 400 K at 25, 150 and 300 MPa

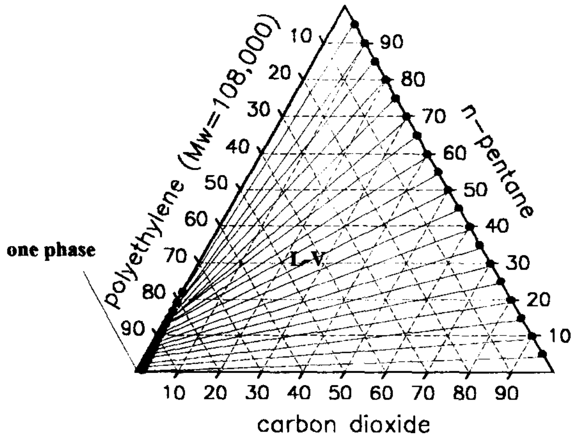

Figure 7 Phase diagram for PE/n-pentane/CO$_2$ system at 460 K and 2 MPa

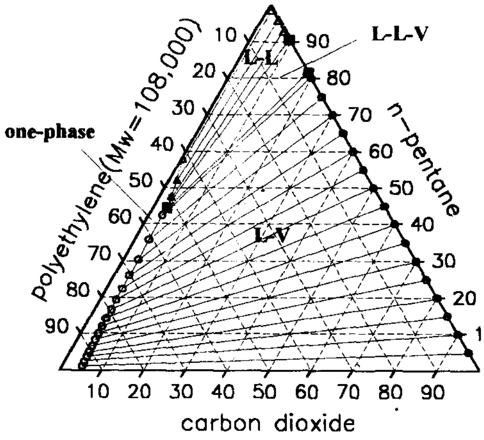

Figure 8 Phase diagram for PE/n-pentane/CO$_2$ system at 460 K and 5 MPa

two-phase region dominates the whole phase diagram in *Figure 7* since pressure is not high enough to introduce any immiscibility for n-pentane/carbon dioxide mixture, which would lead to the formation of a three-phase region.

When pressure is increased to 5 MPa, as shown in *Figure 8*, a three-phase region is indeed detected. The one-phase region in this figure is still small and limited to low carbon dioxide concentration. With a further increase in pressure to 10 MPa (*Figure 9*), the three-phase region is diminished. This trend with pressure is the same as before, but the disappearance of the three-phase region had been at even higher pressures at lower temperatures.

From the above discussions, the pressure effect on the miscibility of the polyethylene in the n-pentane/carbon dioxide mixtures shows a simple trend, that is, increasing the pressure always leads to the expansion of the one-phase region. A point in the multiphase region at a lower pressure will fall in the one-phase region at a higher pressure.

Analysis of the system behaviour at the same pressure but different temperatures points to an interesting effect of temperature. *Figures 10* to *12* show the comparisons of the phase diagrams at two temperatures (400 and 460 K) at 30, 60 and 100 MPa pressures. As shown in *Figure 10*, at 30 MPa, increasing the temperature leads to the shrinking of the one-phase region. A point in the one-phase region at 400 K may fall into a two-phase region at higher temperature, i.e. at 460 K. This means that a ternary mixture of specific composition may undergo phase separation upon increasing the temperature. This is the well known *LCST* (lower critical solution temperature) behaviour.

The *LCST* nature of this polymer–solvent system changes with pressure. At 60 MPa (*Figure 11*), the

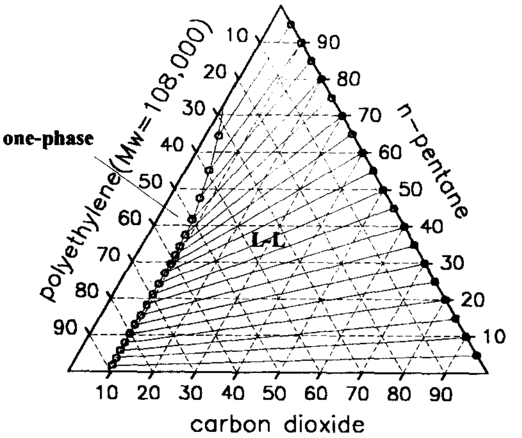

Figure 9 Phase diagram for PE/n-pentane/CO$_2$ system 460 K and 10 MPa

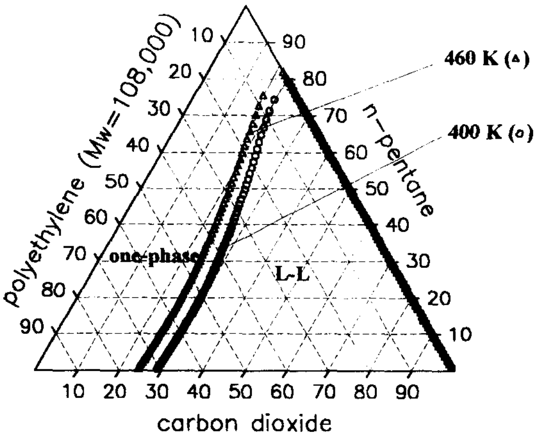

Figure 10 Comparison of phase diagrams of PE/n-pentane/CO$_2$ system for different temperatures at 30 MPa

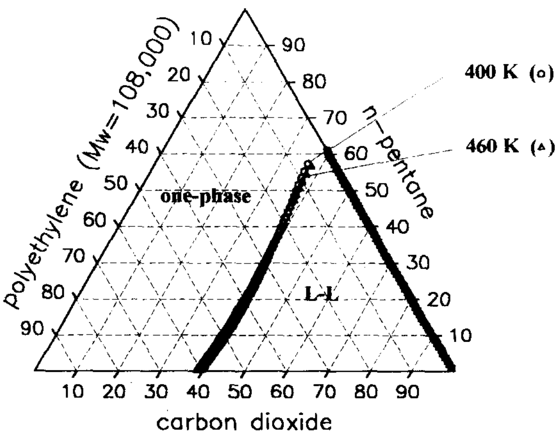

Figure 11 Comparison of phase diagrams of PE/n-pentane/CO$_2$ system for different temperatures at 60 MPa

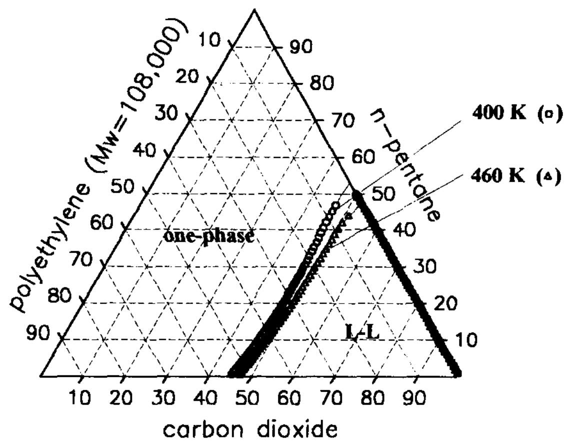

Figure 12 Comparison of phase diagrams of PE/n-pentane/CO$_2$ system for different temperatures at 100 MPa

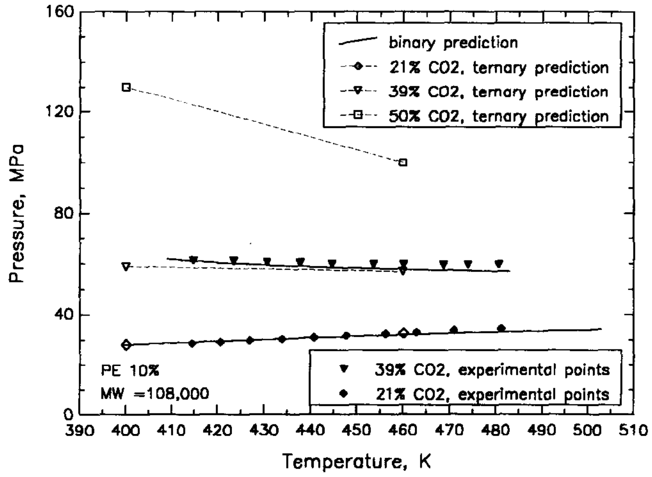

Figure 13 Demixing pressures for 10% by weight PE ($M_w = 108\,000$, $M_w/M_n = 1.32$) solutions in the n-pentane/CO$_2$ binary solvents

influence of temperature on the location of the phase boundary over this temperature range becomes small. As the pressure is increased to even higher values (100 MPa, *Figure 12*), the one-phase region begins to shrink, but now with increasing temperature, which is exactly the opposite to the trend observed at lower pressures. Now the system undergoes phase separation upon a decrease in temperature. This type of behaviour is characteristic of systems showing *UCST* (upper critical solution temperature). Thus, with increasing pressure (which accompanies an increase in the carbon dioxide content in the mixtures), a transition from *LCST* to *UCST* type behaviour takes place.

This transition has been reported in our previous publications[11–13], which present the experimental data and the results of theoretical predictions based on treating the solution as a binary solution of polymer and a pseudo-pure solvent. *Figure 13* shows the data and predictions based on the simplified binary assumption at 10% polymer concentration. The figure also includes the results from the present ternary calculations. Since the experimental ternary data correspond to those mixtures of specific compositions, the predicted value must correspond to the temperature and pressure at which the predicted composition is exactly located on the two-phase boundary in the phase diagram. The predictions from ternary phase diagrams at 400 and 460 K are compared in the figure. For solution containing 21% carbon dioxide, the experimental demixing pressure is about 30 MPa, and increases slightly with increasing temperature, as shown in the figure. Ternary predictions (see *Figure 10*) are in very good agreement with the data. For the mixture containing 39% carbon dioxide, the experimental demixing pressures are slightly above 60 MPa and show a slight decrease with increasing temperature within the range from 400 to 500 K. The ternary predictions here also are in close agreement with the experimental values. The negative slope of the demixing curve at this condition is correctly predicted. Ternary prediction for a mixture containing 50% carbon dioxide is also displayed in the figure. The predicted demixing pressure for the mixture is about 100 MPa and shows a greater temperature sensitivity. This is a correct trend since mixtures with high concentration of carbon dioxide always require higher pressures for complete dissolution of this polymer. The reversal of temperature dependence, which the model predicts well, is a result of the transition from the *LCST* type to *UCST* type behaviour upon increasing the carbon dioxide content in the mixture[12].

FURTHER DISCUSSION

The validity of the assumption that the polymer-lean phase does not contain any polymer needs to be examined. This would be in error for solutions near critical polymer concentrations. We have therefore done calculations without invoking this assumption when critical polymer concentrations are approached. Now both the polymer-rich and the polymer-lean phase are assumed to contain polymer.

Results are shown in *Figures 14* and *15*. *Figure 14* shows the results of these predictions at 400 K and 50 MPa for a polymer of 108 000 molecular weight. The figure also includes the predicted values from the calculations in which polymer-lean phase was assumed to be free of polymer. There is essentially no difference between these two approaches at this molecular weight, indicating that polymer-lean phase must indeed be essentially free of polymer.

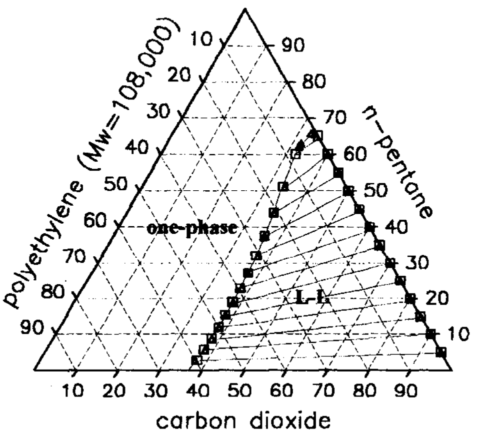

Figure 14 Comparisons of simplified ternary calculations and rigorous ternary calculations for polymer samples with $M_w = 108\,000$ and $M_w/M_n = 1.32$. (□) Simplified calculation (with the assumption that no polymer is present in the polymer-lean phase). (Δ) Rigorous calculation (polymer is assumed to be present in both phases)

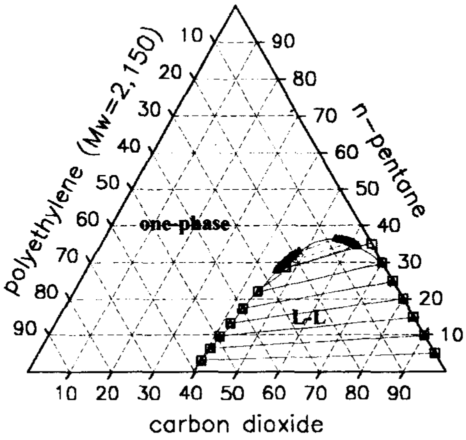

Figure 15 Comparisons of simplified ternary calculation and rigorous calculation for the polymer sample with $M_w = 2150$ and $M_w/M_n = 1.16$. (□) Simplified ternary calculation. (△) Rigorous ternary calculation

Figure 15 shows the results of similar calculations for a polymer of lower molecular weight $M_w = 2150$ ($M_w/M_n = 1.16$), at the same temperature and pressure. Here the results show a difference especially when the critical polymer concentration is approached. This is not unexpected since, near the critical polymer concentration, both polymer-rich and polymer-lean phases are expected to contain measurable amounts of polymer. This becomes more apparent with the low-molecular-weight polymer sample, since the critical polymer concentrations would shift to higher values.

Comparison of *Figures 14* and *15* also provides information on the influence of polymer molecular weight on the extent of one-phase region in the ternary diagrams. As would be expected, with lower-molecular-weight polymer one-phase regions are greater and are entered at lower n-pentane concentrations.

CONCLUSION

The Sanchez–Lacombe lattice-fluid model for polymer solutions has been shown to predict the phase behaviour in polyethylene/n-pentane/carbon dioxide ternary system over a wide range of temperature, pressure and compositions. Calculations have been conducted with or without the assumption that polymer-lean phase contains any polymer. The results essentially have no difference for the polymer with high molecular weight, but differences are observed for the polymer with low molecular weight when the concentrations are close to the critical concentration in the solution.

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