

High-Pressure Phase Behavior in Polyethylene/*n*-Butane Binary and Polyethylene/*n*-Butane/CO₂ Ternary Systems

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SYNOPSIS

Solubility of polyethylene molecular weight standards ($M_w = 2150, 16,400, 108,000,$ and $420,000$ and $M_w/M_n = 1.14, 1.16, 1.32,$ and $2.66,$ respectively) has been studied in near- and supercritical *n*-butane and *n*-butane/CO₂ mixtures at pressures up to 70 MPa. For each polyethylene/solvent system at selected compositions, demixing pressures have been determined using a high-pressure variable-volume view-cell at temperatures up to 200°C. Solutions in pure *n*-butane are found to display LCST (lower critical solution temperature)-type behavior. The behavior of the solutions in *n*-butane/CO₂ mixtures are observed to change from the LCST to the UCST (upper critical solution temperature) with increasing CO₂ content in the binary solvent. Sanchez-Lacombe theory has been used to model these systems. The predictions correctly describe the nature of the phase diagrams for both binary and ternary systems and the calculations are in reasonable agreement with experimental data. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Measurements and predictions of the phase behavior of polymers at high pressures, especially in near- and supercritical fluids, are of growing interest. We have already reported on the solubility of polyethylene molecular weight standards with narrow molecular weight distribution in near- and supercritical *n*-pentane and the mixtures of *n*-pentane/CO₂.^{1,2} We have also reported on the effect of polymer molecular weight, concentration, and solvent composition.^{1,2} It was observed that in the *n*-pentane/CO₂ binary solvents, the behavior of the polyethylene solutions shifts from LCST (lower critical solution temperature)- to UCST (upper critical solution temperature)-type behavior with increasing CO₂ content in the binary solvents. Sanchez-Lacombe theory was used to model these binary and ternary systems and, as reported, the predictions were found to be in very good agreement with the experimental data.^{3,4} The model was capable of predicting the shifts from LCST- to UCST-type behavior.

The present study is focused on the solubility of the same polyethylene samples in pure *n*-butane and in the mixtures of *n*-butane/CO₂ in order to help improve our understanding of the effect of the solvent on the solubility of polymers in high-pressure fluids. In the present article, as before, predictive calculations were conducted using the Sanchez-Lacombe model. Experimental data and model predictions are presented for both the polyethylene/*n*-butane binary and polyethylene/*n*-butane/CO₂ ternary systems. Binary solvent mixtures such as CO₂/*n*-pentane and CO₂/*n*-butane not only permit lowering the critical temperature for the solvent mixtures, but also permit tuning the solubility envelopes for polymers that are important for a wide range of applications from purification and fractionation to processing.⁵

EXPERIMENTAL

Materials

The polyethylene molecular weight standards with narrow molecular weight distributions were obtained from Scientific Polymer Products (Ontario, NY). They are linear polyethylenes produced by hydro-

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Table I Polyethylene Molecular Weight Standards

Molecular Weight (M_w)	Polydispersity (M_w/M_n)
2,100	1.14
16,400	1.16
108,000	1.32
420,000	2.66

generation of polybutadienes. The molecular weight and polydispersities are given in Table I. The solvents, *n*-butane (> 95% purity, obtained from Matheson) and CO₂ (> 99.9% purity, obtained from Liquid Carbonic) were used without further purifications.

Experimental System and Operational Procedure

Demixing pressures (cloud points) were determined using a high-pressure variable-volume view-cell. A detailed description of the apparatus and the operational procedures have been reported in our previous publications.^{1,2} The system is operable at pressures up to 70 MPa and temperatures up to 200°C.

Critical Data

The critical temperature and pressure for *n*-butane and CO₂ are 425.16 K and 3.796 MPa, and for CO₂,

304.19 K and 7.382 MPa, respectively. For the binary mixtures of *n*-butane/CO₂, the critical line is continuous.¹¹ The compositional dependence of T_c and P_c for this binary mixture is shown in Figure 1 as a function of wt % of the alkane in the mixture. As shown, by adding CO₂, the critical temperature can be significantly lowered. Even though the critical temperature lies in between the critical temperatures of the pure components, the critical pressure passes through a maximum that is higher than the pure component values.

MODEL

A detailed description of the Sanchez-Lacombe model can be found in the literature.⁶⁻⁹ It is a lattice-fluid model in which vacancies are introduced to take into account the compressibility and density changes.

The basic equation of state is given by

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

where \tilde{p} , \tilde{T} , and $\tilde{\rho}$ are the reduced pressure, temperature, and density, respectively, and r represents the number of lattice sites occupied by a molecule. The reduced parameters for a pure substance are defined as $\tilde{p} = p/p^*$, $\tilde{T} = T/T^*$, and $\tilde{\rho} = \rho/\rho^*$, where p^* , T^* , and ρ^* are the characteristic pressure, temperature, and density, respectively. For mixtures,

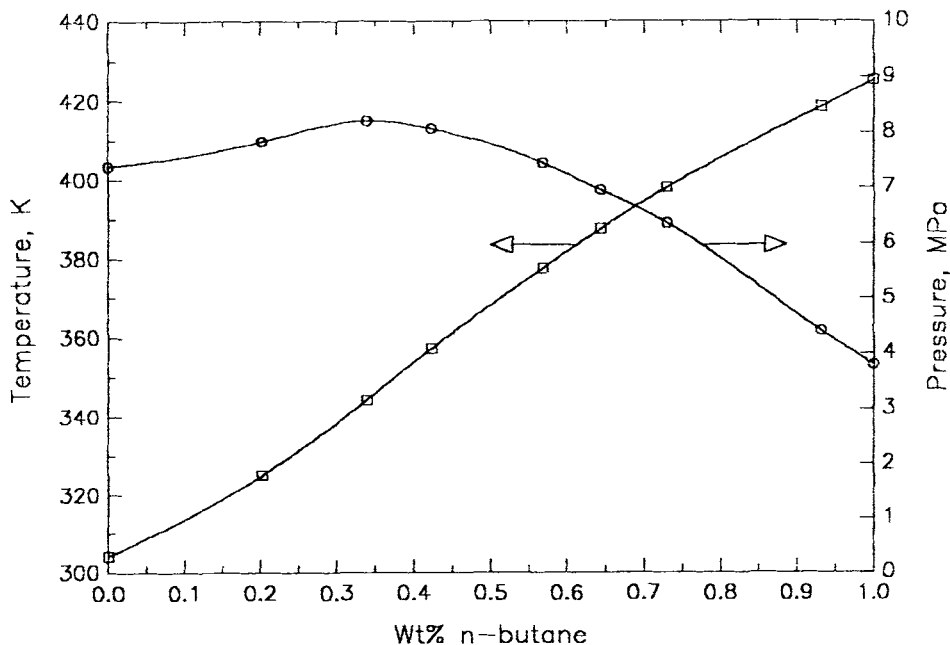


Figure 1 Critical lines for *n*-butane/CO₂ mixtures. (Data from Ref. 6.)

Table II Characteristic Parameters Used in the Modeling

	P^* (MPa)	T^* (K)	ρ^* (g/cm ³)	Reference
<i>n</i> -Butane	322.0	403	0.736	6
Carbon dioxide	574.5	305	1.510	10
Polyethylene	359.0	521	0.895	3, 6

one additional interaction parameter, δ_{ij} , is introduced for each binary pair. This is the only adjustable parameter in the model. The calculation procedure to generate the phase diagrams for polyethylene/solvent systems is as described in our previous publications.^{3,4} The characteristic parameters for each pure substance used in modeling these systems are given in Table II.

RESULTS AND DISCUSSION

Polyethylene/*n*-Butane Binary System

Figure 2 shows the experimental P - T curves for the polyethylene/*n*-butane system for different molecular weight samples at 5% (by weight) polymer con-

centration. The regions below the demixing curves are the two-phase regions, and the regions over these curves are the one-phase regions. As shown in the figure, the demixing pressures always increase with increasing temperature for a given sample. Demixing pressures increase with increasing molecular weight at a given temperature. The vapor-pressure curve for pure *n*-butane, which terminates at the solvent critical point ($T_c = 425.16$ K, $P_c = 3.796$ MPa), is also shown in the figure.

Figures 3-5 show the demixing curves for the polymer sample ($M_w = 108,000$, $M_w/M_n = 1.32$) at different concentrations. The pressure-composition (P - X) and temperature-composition (T - X) diagrams were obtained by taking constant temperature and constant pressure cuts from the P - T curves, respectively. In the P - X diagram (Fig. 4), the region above each curve is the one-phase region at the indicated temperature. In the T - X diagram (Fig. 5), however, the region above the curve is the two-phase region at the indicated pressure. At a given pressure, one-phase regions are entered (i.e., complete miscibility is achieved) upon decreasing the temperature. The system displays an LCST.

Figure 6 shows the comparison of the Sanchez-Lacombe model predictions for the same polymer

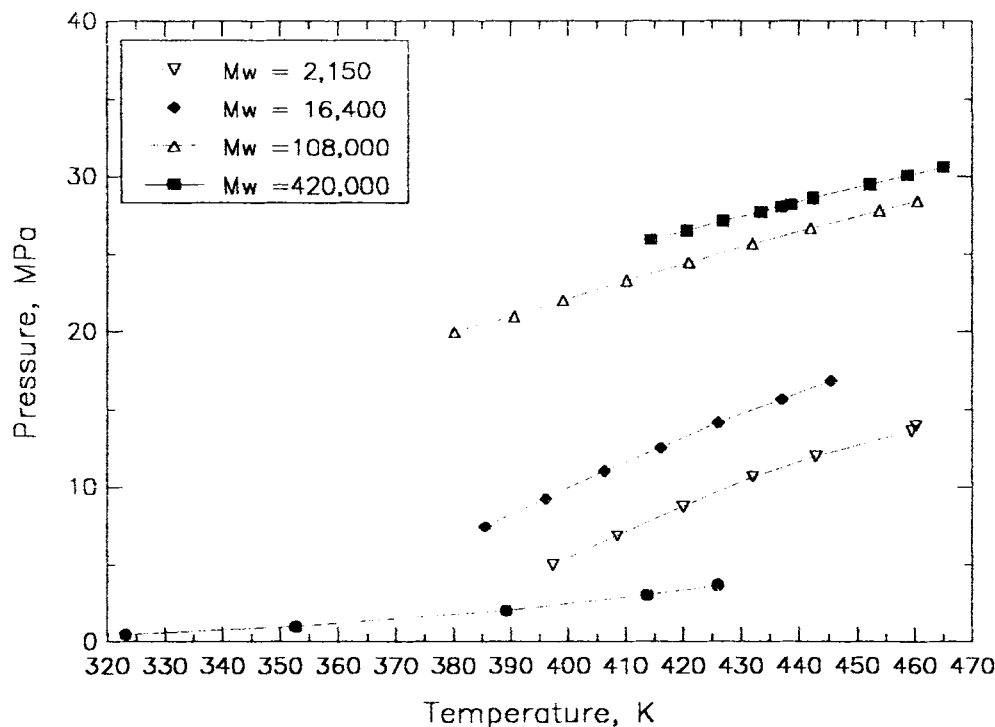


Figure 2 Variation of the demixing pressures with molecular weight for PE solutions (5% by weight) in *n*-butane. The bottom solid line is the L - V equilibrium curve for pure *n*-butane, which ends at its critical point.

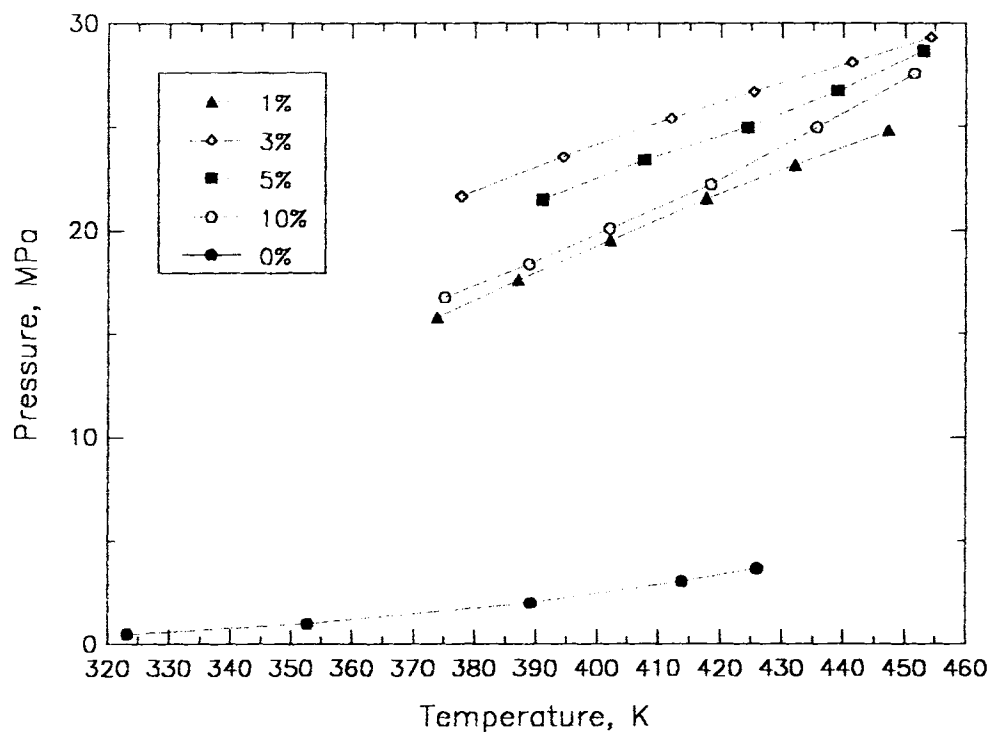


Figure 3 Demixing pressures for PE standard ($M_w = 108,000$, $M_w/M_n = 1.32$) in *n*-butane. 0% stands for the *L-V* equilibrium curve (solid line) for pure *n*-butane, which ends at its critical point.

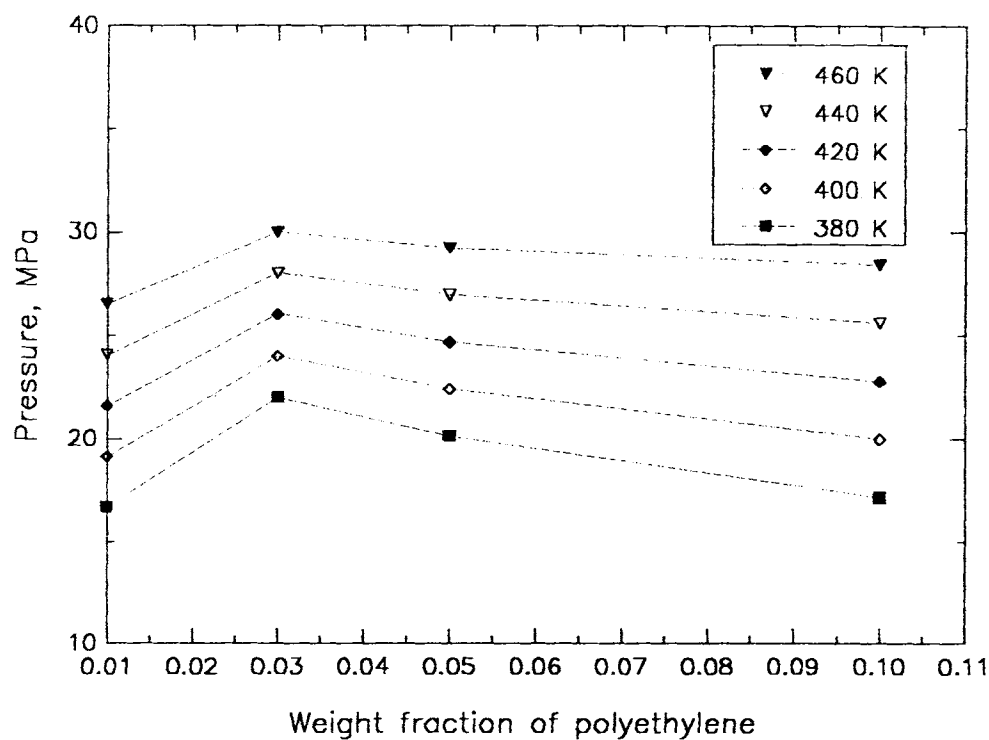


Figure 4 Variation of demixing pressures of PE standard ($M_w = 108,000$, $M_w/M_n = 1.32$) solutions with polymer concentration.

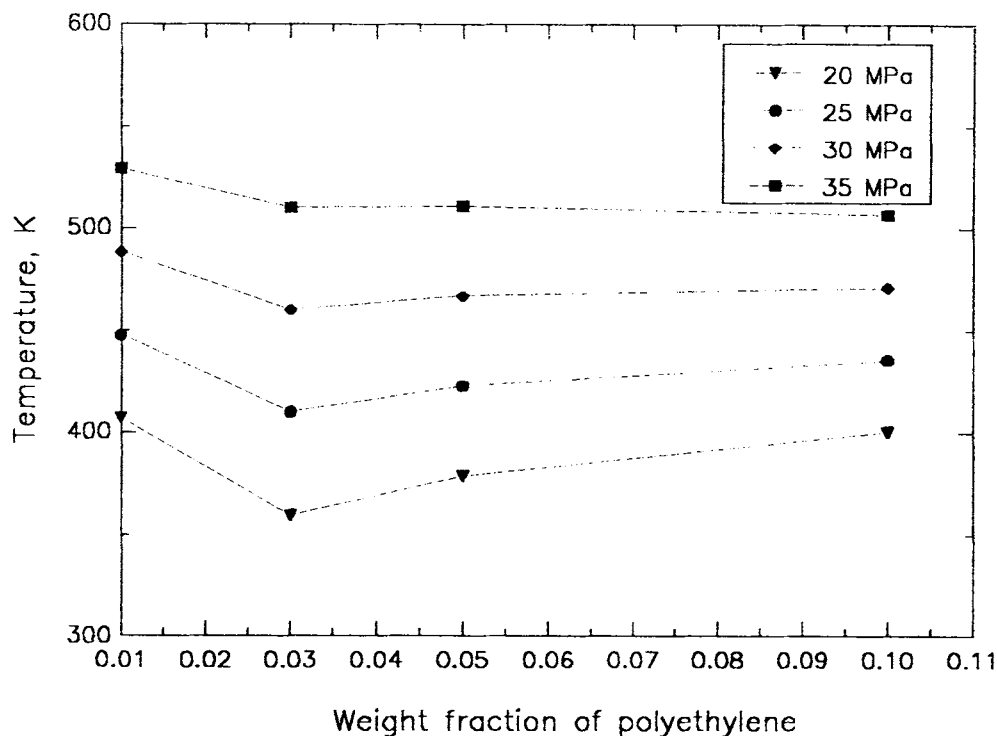


Figure 5 Variation of demixing temperatures of PE standard ($M_w = 108,000$, $M_w/M_n = 1.32$) solutions with polymer concentration.

sample at different concentrations. Initially, the predictive calculations were carried out using a constant value of the interaction parameter $\delta = .0185$, which was obtained by fitting the experimental data at 5% polymer concentration at 460 K. This is the way calculations were conducted to describe the polyethylene/*n*-pentane system.³ The predictions are shown as dashed lines in this figure. The predictions deviate significantly (as much as 5 MPa, see Table III) from the experimental values at temperatures other than 460 K, the temperature at which data were fitted. This observation indicates a strong temperature dependence for δ in these systems. A simple empirical modification was adopted to describe the temperature dependence and therefore improve the accuracy of the predictions. The value of the interaction parameter δ is no longer assumed to be constant but treated as a linear function of temperature. The best fitting values of δ at 460 and 400 K at 5% polymer concentration were used to determine the functional form of the temperature dependence of δ . The solid lines in the figure are the predictions using such temperature-dependent values for the interaction parameter that is given by $\delta = 0.0071 + 2.5 \cdot 10^{-5} T$. By this modification, the predictions are improved significantly over the whole temperature range. The root-mean-

square deviations for these predictions are given in Table III. The worst case is the 1% polymer concentration, which shows an average deviation of about 4 MPa or relative deviation about 21%. The predictions for all the other concentrations are within 2 MPa. Similar analysis with the polyethylene/*n*-pentane system did not show a significant temperature dependence of δ , and the predictions were all within 1 MPa of experimental values.³ It should be pointed out that the characteristic parameter for polyethylene (given in Table II) used in the present calculations was determined by optimizing the predictions using experimental data for polyethylene/*n*-pentane solutions. The predictions for the system polyethylene/*n*-butane system could be improved if the polymer parameters were to be optimized specifically for this system. Further improvement could be achieved by using more appropriate relationships (i.e., nonlinear functions) to describe the variations of δ with temperature or other factors. We did not pursue these in order to assess the value of the predictive capability of the model, which, in principle, should depend only on the pure component characteristic parameters.

Figure 7 shows more explicitly the predictions of the *P*-*X* curves for different molecular weight samples at 460 K. The solid lines are the predicted bi-

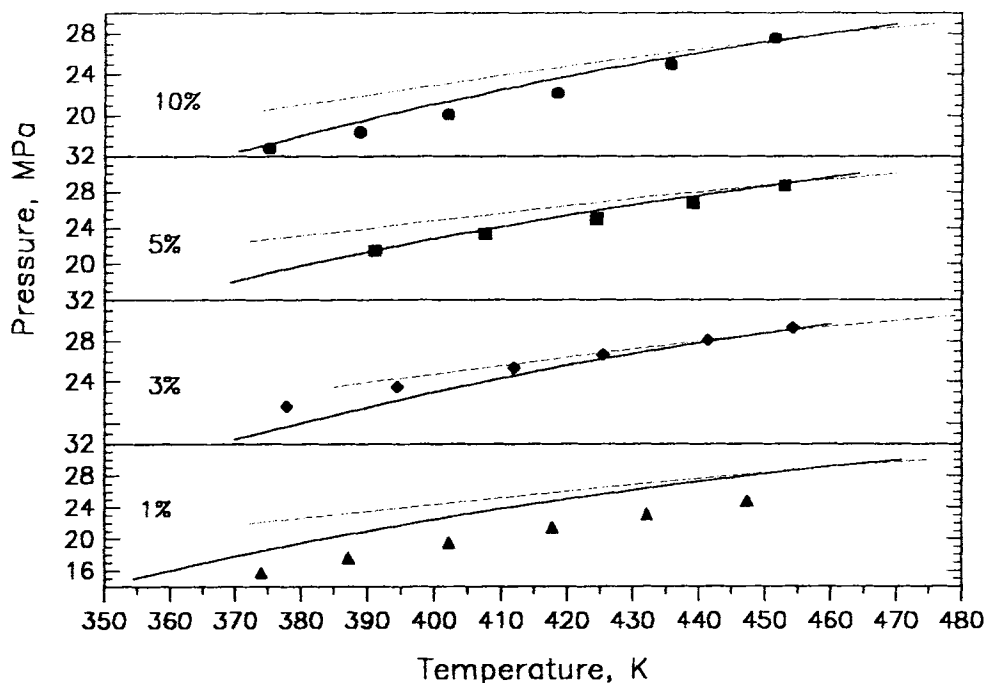


Figure 6 Demixing pressures for PE ($M_w = 108,000$, $M_w/M_n = 1.32$) in *n*-butane. Dashed lines are calculated using a constant $\delta = 0.0185$; solid lines are calculated using $\delta = 0.0071 + 2.5 \cdot 10^{-5} T$.

nodals and the dashed lines are the predicted spinodals. The model correctly predicts the trends in the molecular weight dependence of the solubility.

The positive slopes for P - T curves in Figures 2, 3, and 6 actually indicate that, at a given pressure, phase separation will take place upon increasing temperature, which is a typical feature of systems showing LCST-type behavior. This was shown explicitly in Figure 5. Figure 8 shows the predictions and the experimental values for the T - X curve at 30 MPa for the polymer sample of $M_w = 108,000$. The calculations qualitatively predicts the LCST behavior of the system.

Polyethylene/*n*-Butane/ CO_2 Ternary System

Ternary experiments were carried out for the polyethylene sample of $M_w = 420,000$ ($M_w/M_n = 2.33$) in binary solvent mixtures of *n*-butane/ CO_2 . As pointed out in our previous publication,^{3,4} for high molecular weight polymer samples, the ternary calculations can be simplified by assuming that the polymer-lean phase is essentially free of polymer. This assumption is invoked in all of the present calculations. The experimental P - T data and the results of predictions are shown in Figure 9. Here, again, the regions above each curve corresponds to the one-phase regions.

As in the case of *n*-pentane/ CO_2 systems,¹⁻⁴ adding CO_2 into *n*-butane increases the demixing pressure and the slope of the P - T curve changes from positive at low CO_2 content to negative at high CO_2 content, which indicates that the system behavior shifts from LCST- to UCST-type behavior. For example, in the solvent containing 9.5% CO_2 , the system enters the two-phase region by increasing temperature (i.e., LCST behavior), but in the solvent containing 33.3% CO_2 , one-phase regions are entered upon increase in temperature (i.e., UCST behavior).

Figure 10 shows the model predictions for the phase behavior of the polyethylene(1)/*n*-butane(2)/ CO_2 (3) system at 400 K and 3 MPa. The interaction parameters (δ_{12} , δ_{23} , and δ_{13}) for the three binary branches polyethylene/*n*-butane, *n*-butane/ CO_2 , and polyethylene/ CO_2 are 0.013, 0.13, and 0.1, respectively. The value of δ_{12} was optimized using data for the polyethylene/*n*-butane binary system; the value of δ_{23} was selected using VLE data from the literature⁶ for the *n*-butane/ CO_2 binary system. This is shown in Figure 11. The value of δ_{13} was determined by matching the ternary experimental data. The general feature of the phase diagram is that there is a three-phase region (L - L - V) bounded by two two-phase regions (L - V and L - L). The two-phase region (L - V) starting from low *n*-butane

Table III Root-mean-square Deviation (RMSD)^a and Relative Root-mean-square Deviation (RRMSD)^b of the Predictions for P - T Curves for Polyethylene Solutions ($M_w = 108,000$) in n -Butane

	Polymer Conc'n			
	1%	3%	5%	10%
RMSD (MPa) (for $\delta = \text{constant}$)	5.25	1.16	2.76	3.20
RRMSD (MPa)	26.8%	4.8%	11.7%	15.1%
RMSD (MPa) (for $\delta = 0.0071 + 2.51 \cdot 10^{-5} T$)	3.87	1.45	0.98	1.13
RRMSD (MPa)	21.4%	6.1%	4.2%	5.4%

^a Root-mean-square deviation = $\sqrt{(1/n) \sum_{i=1}^n (p_i^{\text{pred}} - p_i^{\text{exp}})^2}$, where p_{pred} represents the demixing pressure by calculation, p^{exp} represents the experimental data for demixing pressure, and n is the number of data points for the specific curve.

^b Relative root-mean-square deviation = $\sqrt{(1/n) \sum_{i=1}^n [(p_i^{\text{pred}} - p_i^{\text{exp}})/p_i^{\text{exp}}]^2}$.

concentrations describes the equilibrium between the polymer-rich liquid and the polymer-lean vapor phase. The base of the three-phase region is along the n -butane/ CO_2 binary axis and the compositions corresponding to the three-phase envelope correspond to the immiscibility gap in the n -butane/ CO_2 binary mixtures, which is in the range from 92.7 to 98.5% n -butane. (This has been verified from the comparisons with phase diagrams of the n -butane/ CO_2 binary system¹¹ at similar temperature and pressure.) The other two-phase region (L - L) at high

n -butane concentrations describes the equilibrium between the polymer-rich liquid and the polymer-lean liquid phases. The extent of this two-phase region is very small at this temperature and pressure. The one-phase region shown in this figure is also very small and confined to a CO_2 content less than 2%. When temperature is increased to 460 K, no three-phase region can be detected at this pressure. Further, no three-phase region can be identified at 460 K in the pressure range up to 300 MPa. This is not unexpected, because the presence of the three-

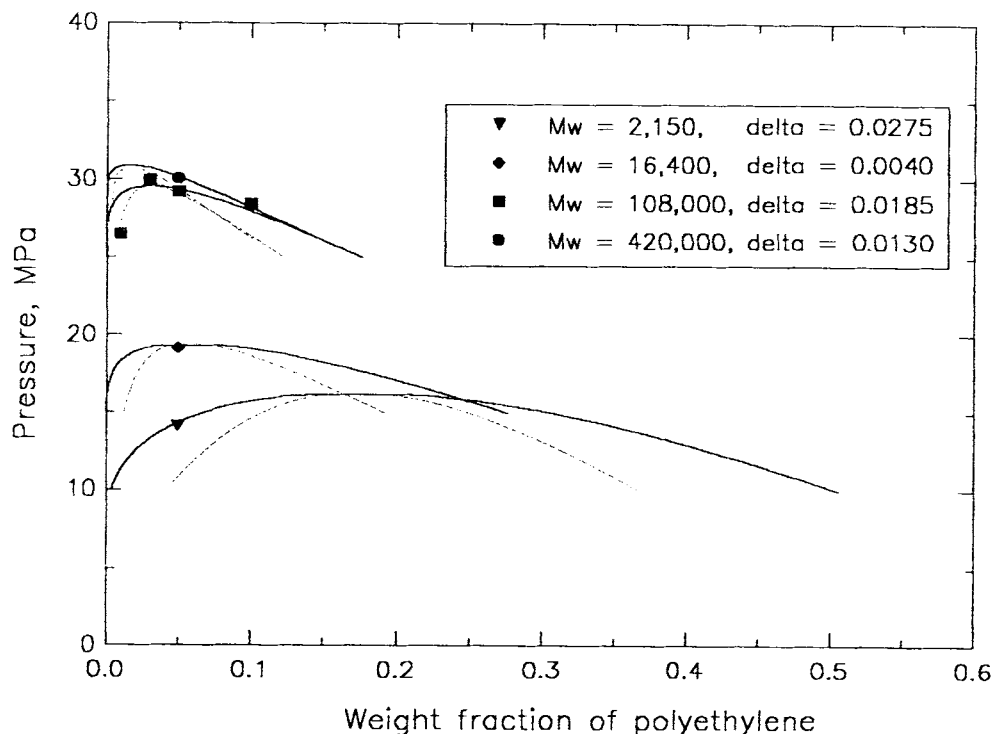


Figure 7 Variation of demixing pressures of PE solutions with polymer concentration and molecular weight at 460 K in n -butane. Solid lines are calculated binodals, and dashed lines are calculated spinodals. Different symbols are experimental points.

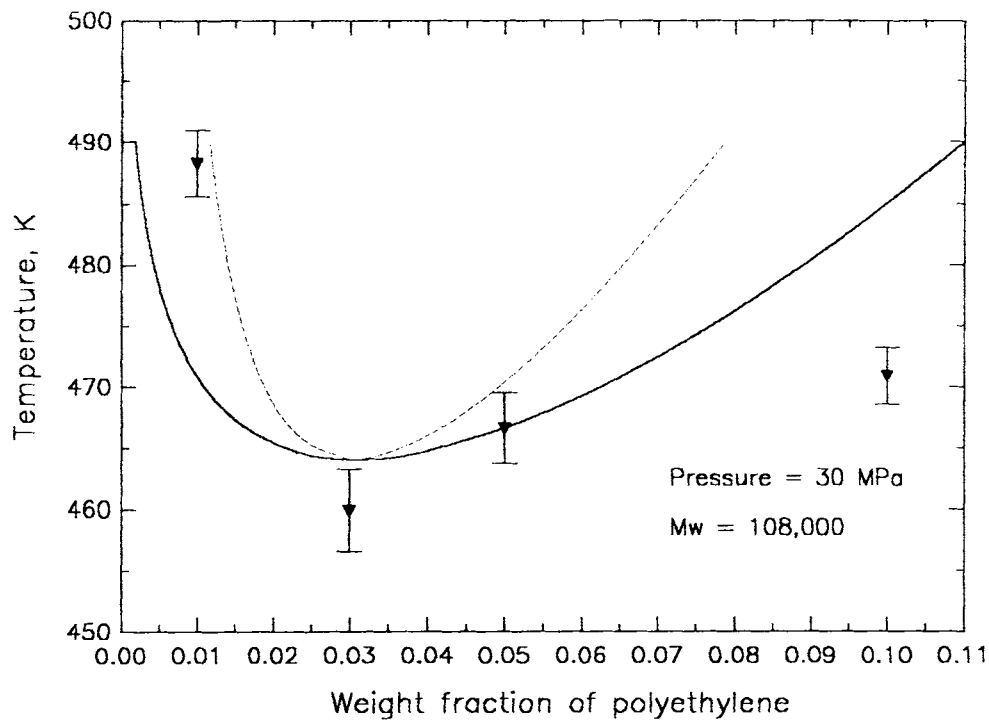


Figure 8 Variation of demixing temperature of PE solutions with polymer concentration in *n*-butane. Solid lines are calculated binodals, and dashed lines are calculated spinodals.

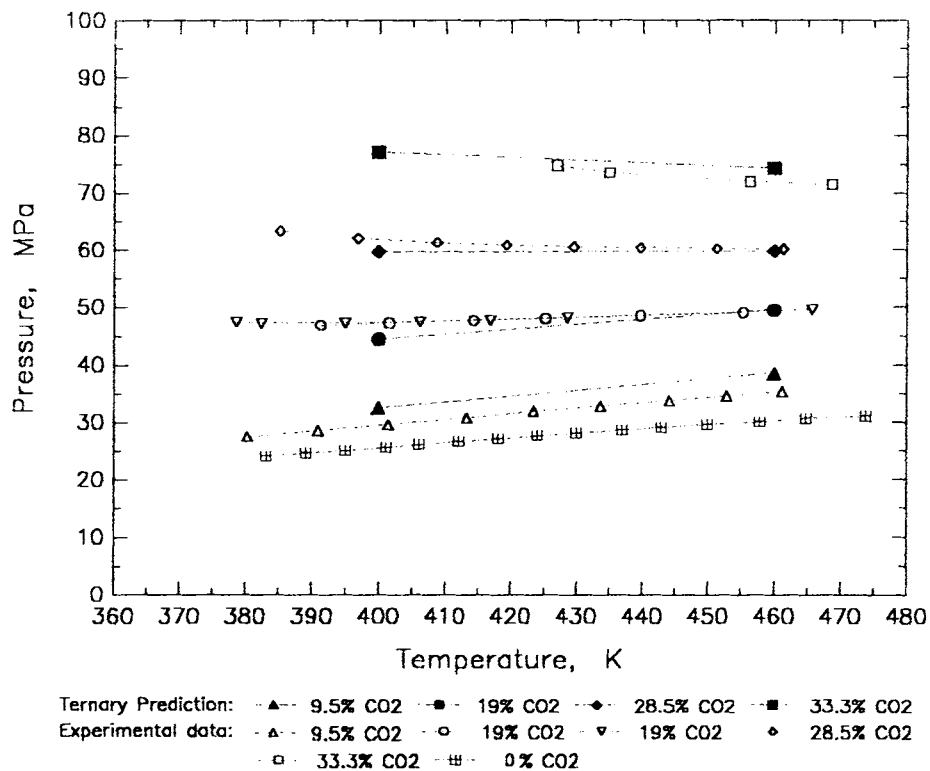


Figure 9 Demixing pressures for 5% by weight PE ($M_w = 420,000$, $M_w/M_n = 2.66$) solutions in the *n*-butane/CO₂ binary solvents.

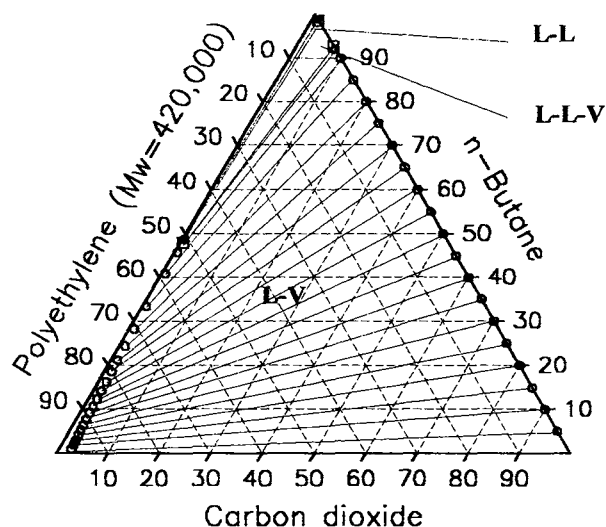


Figure 10 Phase diagram of PE/*n*-butane/CO₂ system at 400 K and 3 MPa.

phase region is related to the immiscibility of the *n*-butane/CO₂ binary mixtures, and at 460 K, no visible immiscibility gap can be detected for the binary system of *n*-butane/CO₂ at any pressure.

Figure 12 shows the comparison of phase diagrams at 460 and 400 K at 10 MPa. The values of

the interaction parameters δ_{12} , δ_{23} , and δ_{13} at 460 K are 0.013, 0.13, and 0.09, respectively. Here, the value of δ_{13} is slightly different from the value used at 400 K. As all the interaction parameters are essentially temperature-dependent, this adjustment is for the purpose of matching the experimental data. As shown in this figure, the three-phase region disappears for both temperatures at this pressure as expected. Even though a one-phase region also exists, the phase diagram is dominated by the liquid-liquid two-phase region. The tie lines connect the polymer-rich and polymer-lean phases. The expansion of the one-phase region at 400 K upon increasing pressure (compare with Fig. 10) indicates that the miscibility of CO₂ in polyethylene/*n*-butane mixtures is increased significantly with pressure. This figure also shows that the one-phase region increases in going from 460 to 400 K. This observation indicates that a point in the one-phase region at 400 K may fall into the two-phase region at 460 K. In other words, phase separation can be achieved upon increasing temperature. This is the LCST-type behavior.

As pressure is increased to 35 MPa (Fig. 13), the one-phase regions expand further for both temperatures (see Figs. 10 and 12). These one-phase regions cover the whole polyethylene/*n*-butane

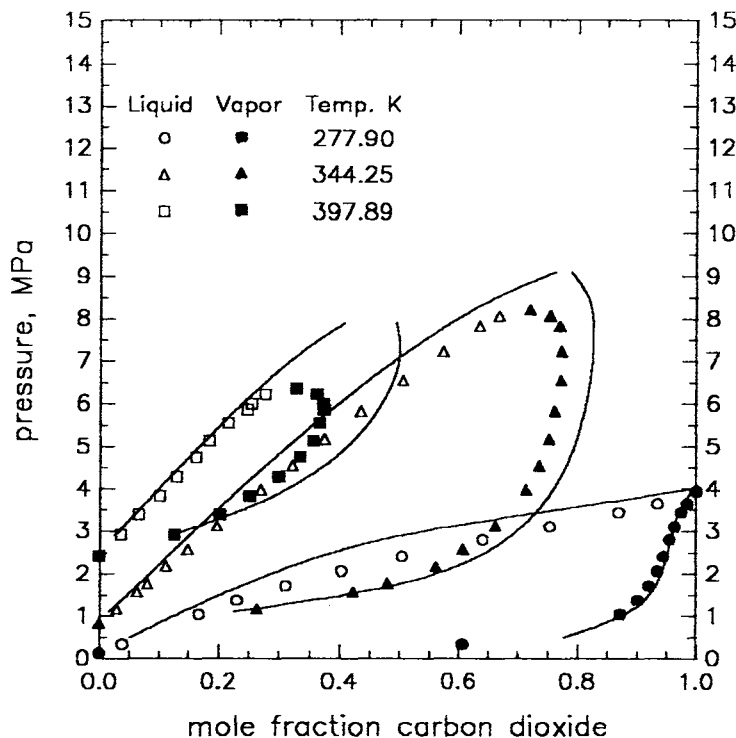


Figure 11 Pressure-equilibrium phase composition diagram for the *n*-butane/CO₂ binary system. Solid lines are the predictions by the Sanchez-Lacombe model. Experimental data points are from the literature.¹¹ $\delta = 0.1$ for all calculations.

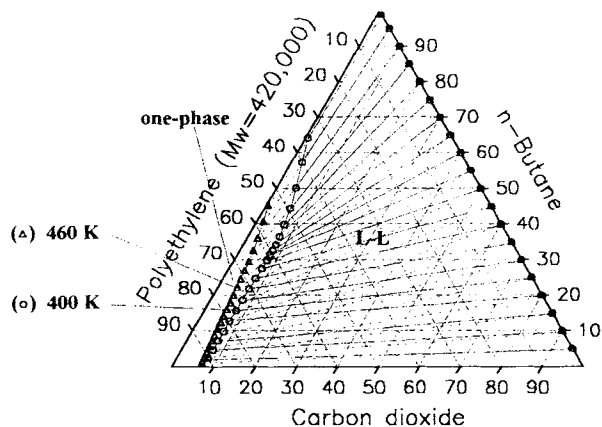


Figure 12 Comparison of phase diagrams of PE/*n*-butane/CO₂ system at 460 and 400 K. Pressure = 10 MPa.

branch, which means complete miscibility can be achieved for the ternary mixtures for any concentration of polyethylene as long as the concentration of CO₂ is low. Though, for the most part, the two-phase region at 400 K is still within the two-phase region at 460 K (typical feature of systems showing the LCST), the phase boundaries cross each other at high polymer concentrations. After the crossover, a system with a high polymer concentration that was in the two-phase region at lower temperature (400 K) now falls into the one-phase region at a higher temperature (460 K). This is the UCST-type behavior. So, at this temperature and pressure, the system is predicted to show both LCST- and UCST-type behavior depending on the polymer concentration in the mixture.

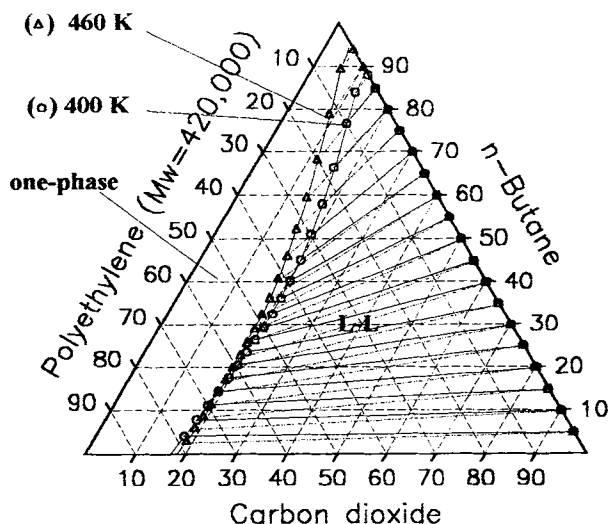


Figure 13 Comparison of phase diagrams of PE/*n*-butane/CO₂ system at 460 and 400 K. Pressure = 35 MPa.

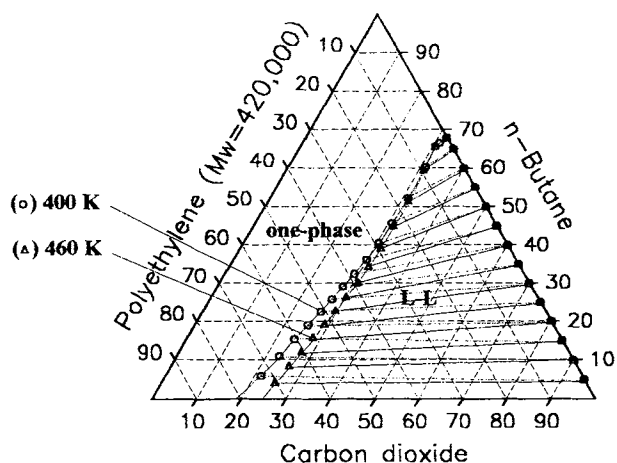


Figure 14 Comparison of phase diagrams of PE/*n*-butane/CO₂ system at 460 and 400 K. Pressure = 65 MPa.

As pressure is increased to an even higher value (65 MPa, Fig. 14), the two-phase region at 460 K is now completely inside the two-phase region at 400 K. Now, UCST-type behavior is displayed at all polymer concentrations. This figure further shows that for the mixtures of low polymer concentrations temperature change has essentially no influence on the position of the phase boundary. This phenomenon means that the demixing pressure would be relatively constant at the present temperature range, which, as will be discussed later in this section, is in good agreement with the experimental observations.

Figure 15 shows a comparison of the phase diagrams at 460 and 400 K at 80 MPa. The two-phase

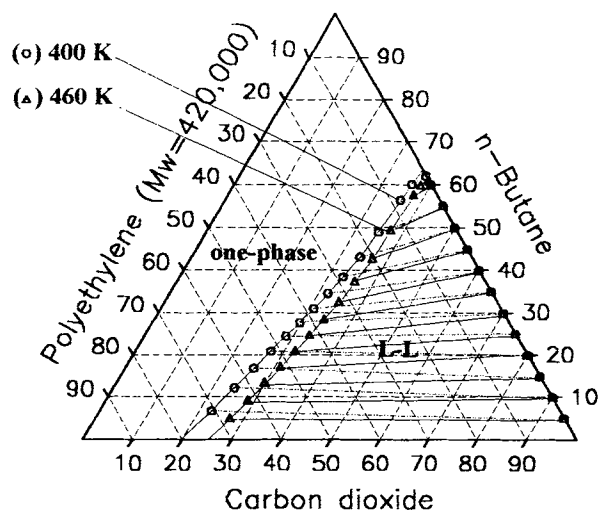


Figure 15 Comparison of phase diagrams of PE/*n*-butane/CO₂ system at 460 and 400 K. Pressure = 80 MPa.

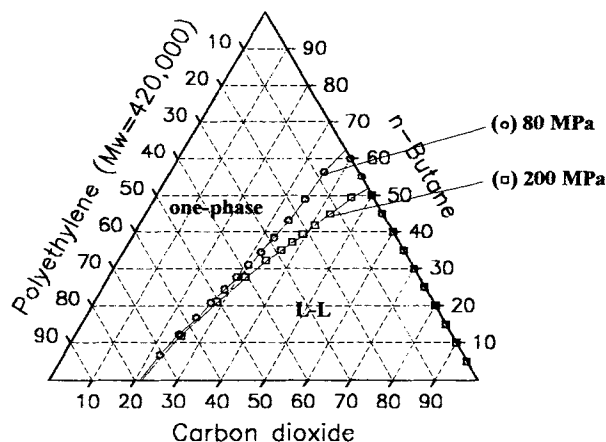


Figure 16 Phase diagrams of PE/*n*-butane/ CO_2 system at 80 and 200 MPa. Temperature = 400 K.

region at 460 K now is obviously smaller than that at 400 K. UCST-type behavior could be observed more easily even at a low polymer concentration. The one-phase regions are now much larger than those at lower pressures. This expansion upon increasing pressure continues to even higher pressures up to 200 MPa. This is shown in Figure 16 for the temperature of 400 K.

The predictions from the present calculations have been made at only two temperatures. They are compared with experimental data in Figure 9. As

shown in this figure, they are in reasonable agreement with experimental values. UCST and LCST transitions are also correctly predicted.

FURTHER DISCUSSION

Figure 17 shows the comparison of the demixing pressures for the polyethylene sample ($M_w = 108,000$, $M_w/M_n = 1.32$) in *n*-butane and *n*-pentane. Compared to *n*-pentane, *n*-butane is not as good a solvent, and the demixing pressures are nearly doubled in going from *n*-pentane to *n*-butane. Similar behavior was also observed for the other molecular weight polyethylene samples.

SUMMARY AND CONCLUSION

Polyethylene solutions in pure *n*-butane display LCST behavior. In polyethylene/*n*-butane/ CO_2 ternary systems, the miscibility of CO_2 in the polyethylene/*n*-butane mixtures decreases upon increasing the CO_2 content in the mixture. (The mixtures with a high concentration of CO_2 always require higher pressures for complete dissolution of the polymer.) This transition takes place first at relatively low pressures for mixtures of high polymer

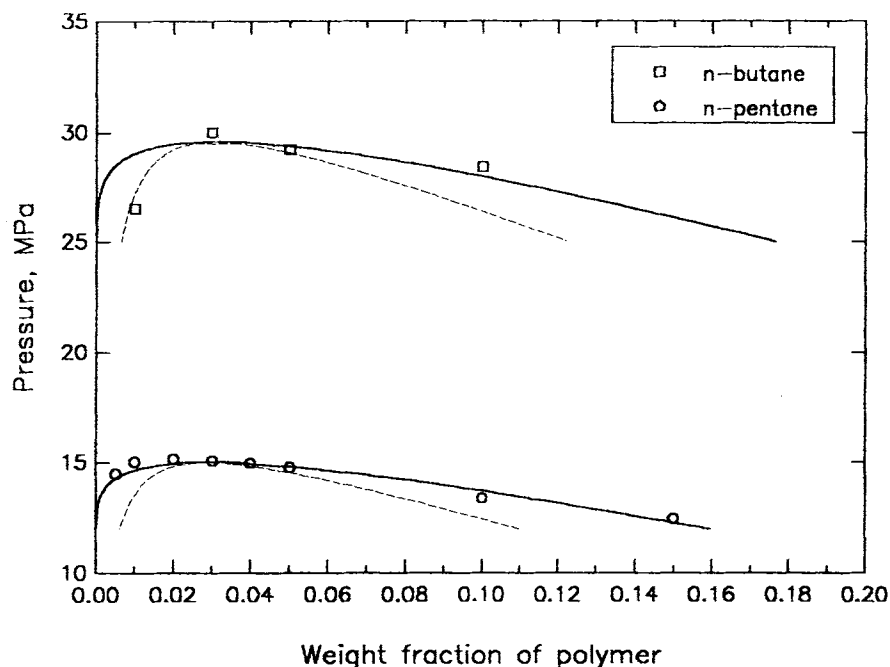


Figure 17 Comparison of demixing pressures of PE solutions ($M_w = 108,000$, $M_w/M_n = 1.32$) at 460 K in *n*-butane and *n*-pentane. Symbols are experimental data, solid lines are calculated binodal curves, and dashed lines are calculated spinodal curves.

concentrations and, then, at high pressures, extends to mixtures of low polymer concentration.

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