

Solubility and Demixing of Polyethylene in Supercritical Binary Fluid Mixtures: Carbon Dioxide–Cyclohexane, Carbon Dioxide–Toluene, Carbon Dioxide–Pentane

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SYNOPSIS

Solubility of polyethylene in three different supercritical binary solvent systems—carbon dioxide–cyclohexane, carbon dioxide–toluene, and carbon dioxide–pentane—have been studied. Solvent compositions that lead to complete dissolution at pressures below 70 MPa have been identified. Demixing pressures have been determined for a range of polymer concentrations at temperatures up to 200°C. It is shown that the behavior of the solutions depends strongly on the fluid composition. In the composition ranges studied, solutions in cyclohexane–carbon dioxide mixtures were found to show lower critical solution temperature (LCST) behavior. It is found that the behavior of solutions in carbon dioxide–toluene and carbon dioxide–pentane mixtures shifts from upper critical solution temperature (UCST) to LCST with increasing toluene or pentane content. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Solubility of polymers in supercritical fluids is of growing interest. This is because the properties of supercritical fluids can be easily adjusted for specific needs and customized process solvents can be generated. Even though supercritical fluids involve high pressures, they offer special advantages. Using these fluids, chemical or physical transformations can be fine-tuned while satisfying various stringent requirements, such as temperature stability, environmental acceptability, and ease of solvent or product recovery, that may not easily be met with an ordinary solvent.

Since many applications of supercritical fluids involve either dissolution or precipitation stages, the solubility and demixing behavior of a given substance in a supercritical fluid constitute the starting data base. For polymer systems, such information must be related to the type of the polymer, molecular weight, molecular weight distribution, concentration, and the nature of the solvent. Our research

group has been active for a number of years in investigating these factors. We have been evaluating both pure and binary fluids using either the pressure, or the temperature, or the fluid composition as adjustable tuning parameters in bringing about dissolution of phase separation in selected polymer–fluid systems.^{1–6}

Solubility of polyethylene in supercritical fluids, in particular supercritical ethylene, has already received considerable attention.^{7–22} This is because in the production of low-density polyethylene (i.e., the high-pressure polyethylene process), polymerization proceeds under supercritical conditions. Solubility of polyethylene in a series of supercritical *n*-alkanes including *n*-pentane^{7,23} and other solvents such as fluorotrichloromethane²¹ have also been studied. These studies all report that at sufficiently high pressures, polymer and the solvent show complete miscibility; however, the temperature dependence of solubility shows differences. Specifically, solutions of polyethylene in ethylene are observed to display upper critical solution temperatures (UCST), whereas solutions in *n*-alkanes show lower critical solution temperature (LCST).^{7,23–26} Solutions in fluorotrichloromethane also show LCSTs.^{21,27}

Despite many studies in pure fluids, there are no

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published reports on the solubility behavior of polyethylenes in binary supercritical fluids.

The present study deals with the solubility of polyethylene in the binary fluid mixtures carbon dioxide–cyclohexane, carbon dioxide–toluene, and carbon dioxide–pentane. By changing the carbon dioxide content of the binary, not only the solvent quality, but also the critical temperature and pressure of the mixture fluid are manipulated. The study has been conducted to determine the extent of carbon dioxide that could be tolerated in these mixtures while still achieving complete dissolutions below 70 MPa (upper pressure limit of the experimental system used) and then to determine how changing the solvent characteristics affects the behavior of the solutions.

EXPERIMENTAL

Materials

A polyethylene sample with a molecular weight ($M_w = 121,000$) and a polydispersity ($M_w/M_n = 4.3$), and a crystalline melting temperature of 405 K, as determined by gel permeation chromatography (GPC) and differential scanning calorimetry (DSC) analyses, were used throughout the study. Cyclohexane and pentane (each of 99.9% purity, obtained from Aldrich), toluene (99.9% purity, obtained from Fisher), and carbon dioxide (99.9% purity, obtained from Liquid Carbonic) were used without further purifications.

Experimental System

A schematic diagram of the experimental system is shown in Figure 1. It consists of a variable-volume view cell, a solvent delivery line, and a pressure generation line. The cell is equipped with two sapphire windows for visual observations. Cell content is mixed with a magnetic stirrer. At a given temperature, the cell volume and hence the pressure is changed by moving the piston inside the variable volume part of the cell. Even though some modifications have been made in the design of the cell, functional features of the system are similar to those described in our previous publications.^{1,5} It is operable at pressures up to 70 MPa and temperatures up to 200°C.

Procedure

In a typical experiment, an accurately weighed amount of the polymer is first loaded into the cell.

This is followed by the addition of a measured amount of the liquid solvent, cyclohexane, toluene, or pentane. The cell is then sealed and the desired amount of carbon dioxide is loaded by pumping through the solvent line. The total amount of carbon dioxide addition is determined by weighing the cell before and after the addition is made.

After the loading process is completed, the cell temperature and the pressure is brought to the desired conditions and the cell content is observed over a 10–12 h period through the sapphire windows for indications of swelling and dissolutions. Pressure is manipulated by moving the piston with the pressure generator (PGN) to establish the one-phase conditions. The system is fully equilibrated before taking any data on demixing pressures.

The demixing pressure is determined by repeated cycling through the phase separation and dissolution point at a given temperature. When temperature is changed to a new value, initial long equilibration times are not needed and readings are taken after relatively short equilibration times. In this fashion, for a given polymer concentration and solvent mixture, demixing pressures are determined at all temperatures of interest.

Critical Properties of the Mixtures

Critical temperatures and pressures for the mixtures of carbon dioxide with cyclohexane, toluene, and pentane have been reported in the literature.^{28–30} They have been plotted in Figures 2 and 3 as a function of the weight percent hydrocarbon present in the mixture. As shown in the figures, the behavior is that of simple binary mixtures and the critical lines are continuous. Pure component critical properties are shown in Table I. The critical temperatures of the mixtures lie between the critical temperatures of the pure components, but the critical pressures pass through a maximum which is higher than the critical pressures of the pure components. By addition of carbon dioxide to either cyclohexane, toluene, or pentane, critical temperatures are significantly lowered.

In the present study, the pressures that have been investigated are all above the critical pressures of the binary mixture used. Temperatures are near and above the critical.

RESULTS AND DISCUSSION

Table II summarizes the overall solubility trends as a function of polymer concentration and the hydro-

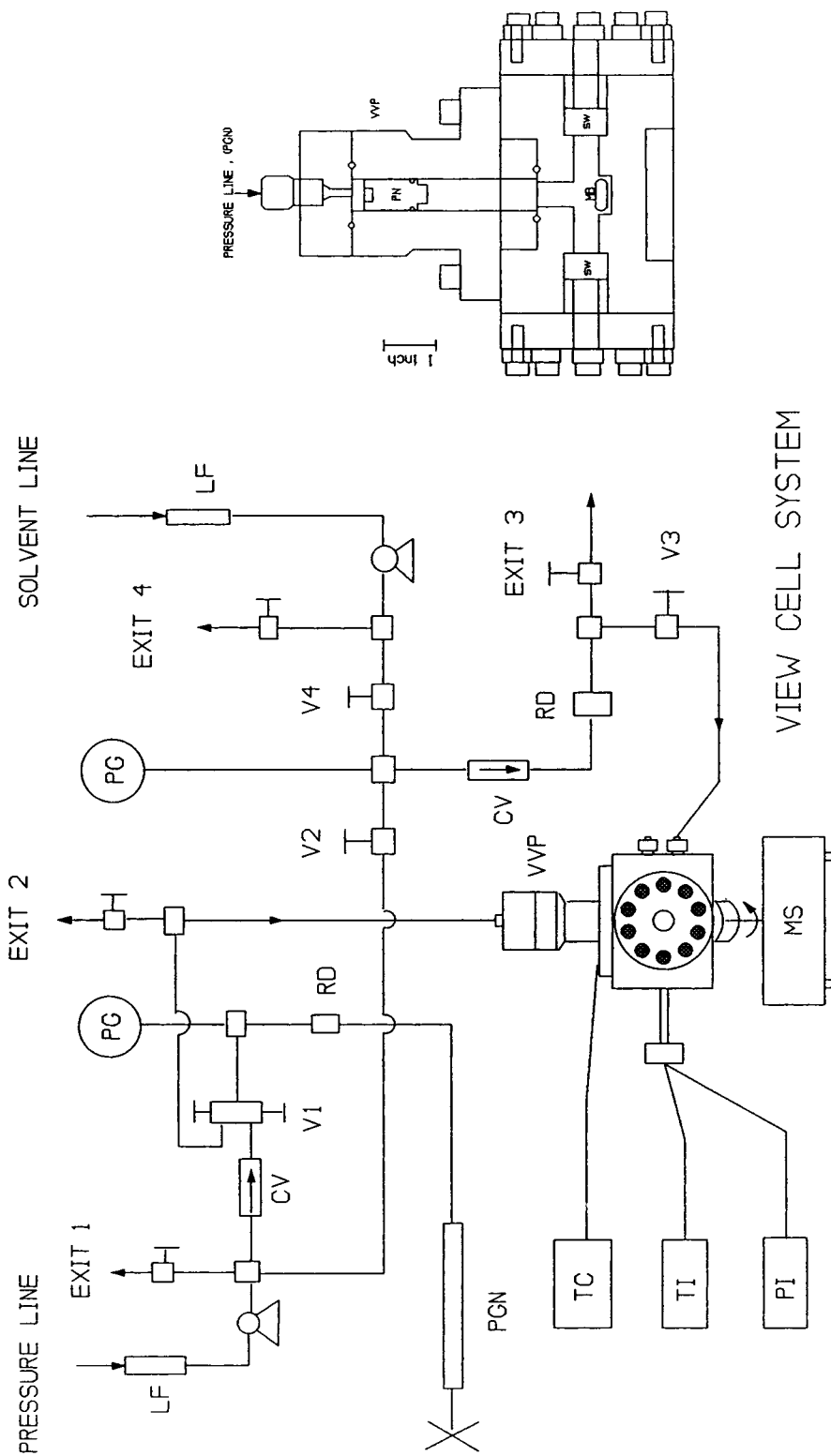


Figure 1 Experimental system. [LF = line filter, CV = check valve, PG = pressure gage, PGN = pressure generator, TC = temperature controller, TI = temperature indicator, PI = pressure indicator, VVP = variable-volume part of the view cell, MS = magnetic stirrer, RD = rupture disc, PN = movable piston, SW = sapphire window, MB = magnetic stirring bar].

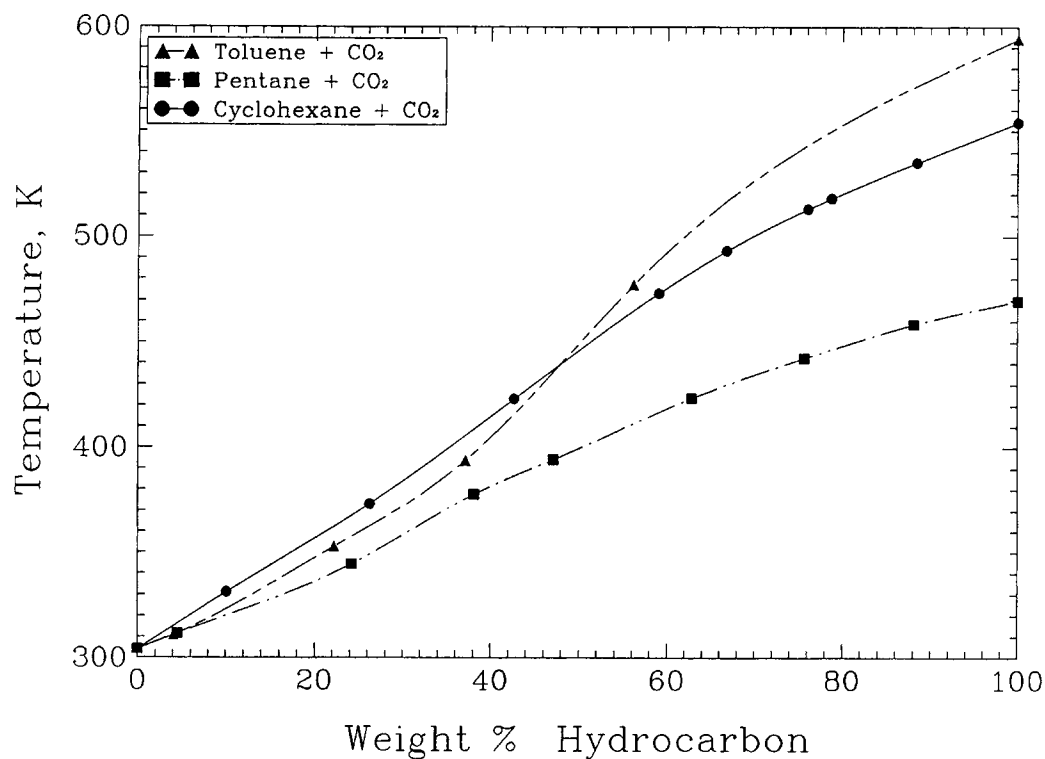


Figure 2 Critical temperatures for the carbon dioxide–hydrocarbon binary mixtures.

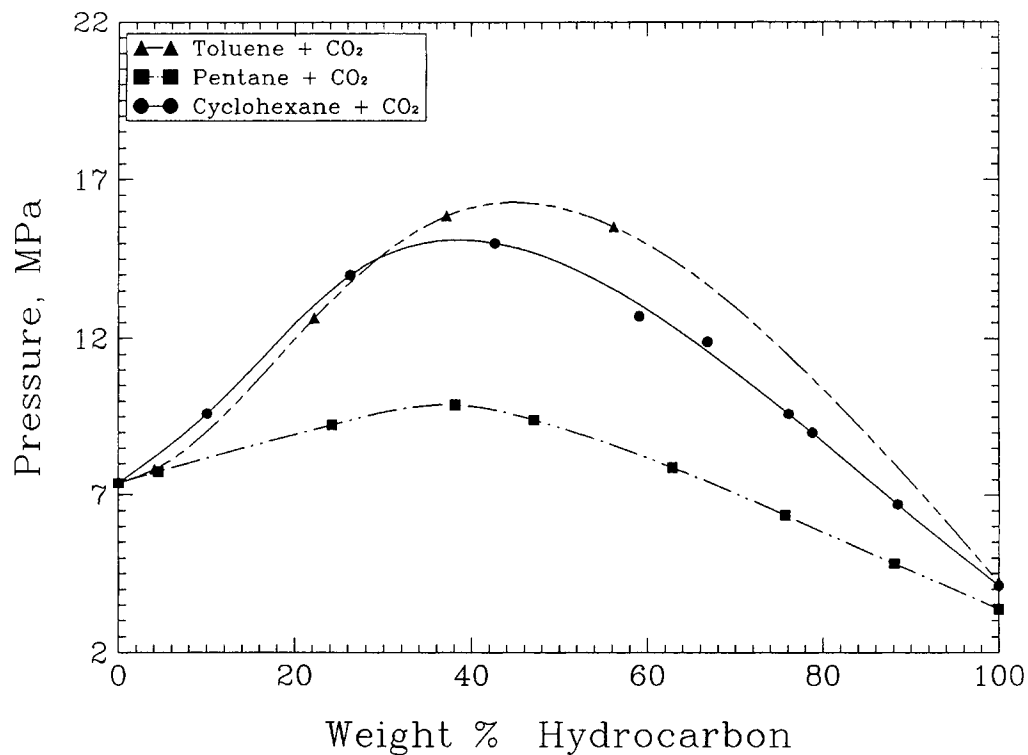


Figure 3 Critical pressures for the carbon dioxide–hydrocarbon binary mixtures.

Table I Critical Properties of Pure Fluids

Compound	T_c (K)	P_c (MPa)
Carbon dioxide	304.21	7.38
Cyclohexane	554.15	4.11
Toluene	593.95	4.21
Pentane	469.56	3.36

carbon content of the binary solvent mixture. For some polymer concentrations, solubility observations are included for two solvent compositions. One of these dissolves the polymer completely at pressures below 70 MPa. The minimum amount of hydrocarbon required to lead to complete dissolution lies between these compositions.

Note that complete dissolutions occur at pressures below 70 MPa, when the cyclohexane or toluene content of the binary mixture is greater than 50, and pentane content is greater than 60% by weight. The amount of hydrocarbon required to achieve complete dissolution becomes higher with higher polymer concentrations.

Solubility in Carbon Dioxide–Cyclohexane Binary Mixture

Figure 4 shows the demixing pressures for 3% by weight polymer solution in binary solvent mixtures

containing different amounts of cyclohexane. Polymer concentrations refer to the amount in the solution. Cyclohexane amount refers to its weight percentage in the carbon dioxide–cyclohexane binary solvent, not in the solution. Figure 5 is a similar figure for the case where polymer concentration is 9% by weight.

In these figures, the regions above each curve are the one-phase regions. As shown the demixing pressures are significantly influenced by the cyclohexane content and are lowered with increasing amount of cyclohexane in the mixture. It is also noted that $(dP/dT)_c$ is positive and the demixing pressures increase with temperature. At a given pressure, two phase regions are entered upon increase in temperature. This is typical of LCST-type behavior.

The LCST-type behavior was observed also at other polymer concentrations that were investigated. This is shown in Figure 6, which is a comparative plot of the demixing pressures for solutions containing 3, 9, 15, and 20% by weight polymer. Even though the solvent compositions are not exactly the same, the usual trends that would be expected with polymer concentration may be noted, that is, the demixing pressures would initially increase with increasing polymer concentration, and beyond a certain concentration (which would be the critical polymer concentration in case of monodisperse polymers) start to decrease. The critical polymer

Table II Screening Tests for Complete Solubility

Nominal Polymer Concentration (wt % of Total)	Hydrocarbon Concentration (wt % in Binary Solvent)	Maximum Temp (K) Tested	Complete Solubility
<i>Carbon dioxide–cyclohexane</i>			
3	47.9	480	No
	53.3	475	Yes
9	49.3	483	No
	57.0	475	Yes
15	52.9	480	No
	65.0	475	Yes
20	58.9	475	Yes
<i>Carbon dioxide–toluene</i>			
3	44.8	480	No
	50.0	480	Yes
9	53.0	475	Yes
	59.0	475	Yes
<i>Carbon dioxide–pentane</i>			
3	60.0	480	No
	62.0	480	Yes
9	63.0	480	Yes

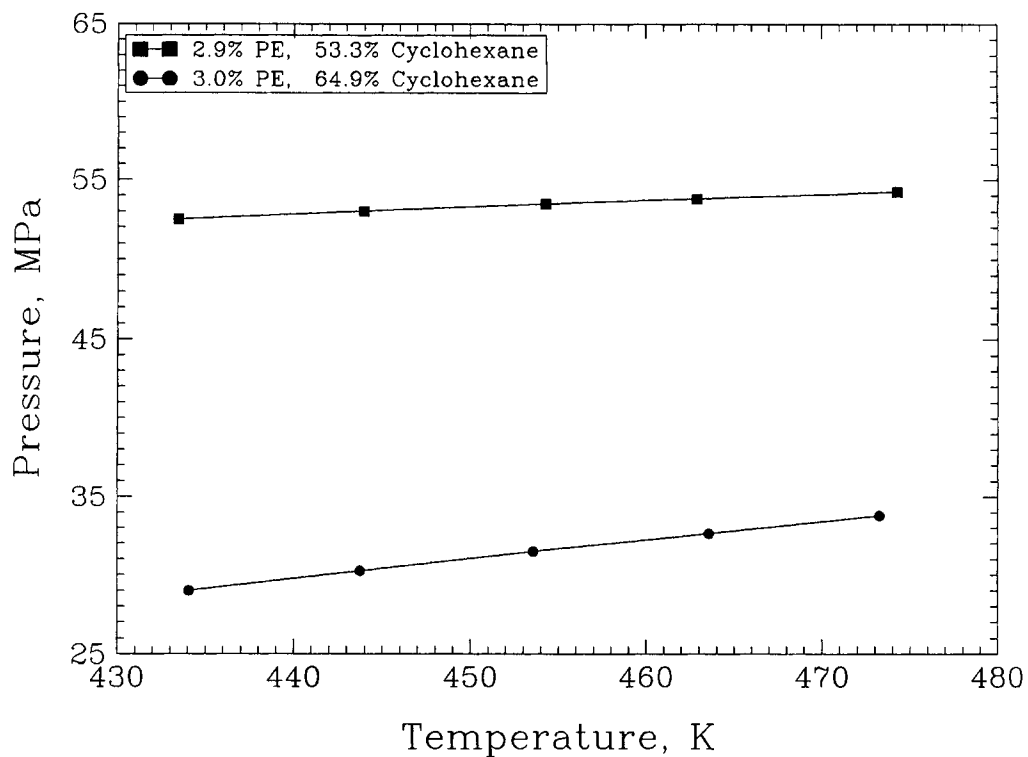


Figure 4 Demixing pressures for 3% by weight polyethylene solutions in the carbon dioxide-cyclohexane binary solvents. (Cyclohexane contents refer to their wt % amounts in the binary solvent, not the solution.)

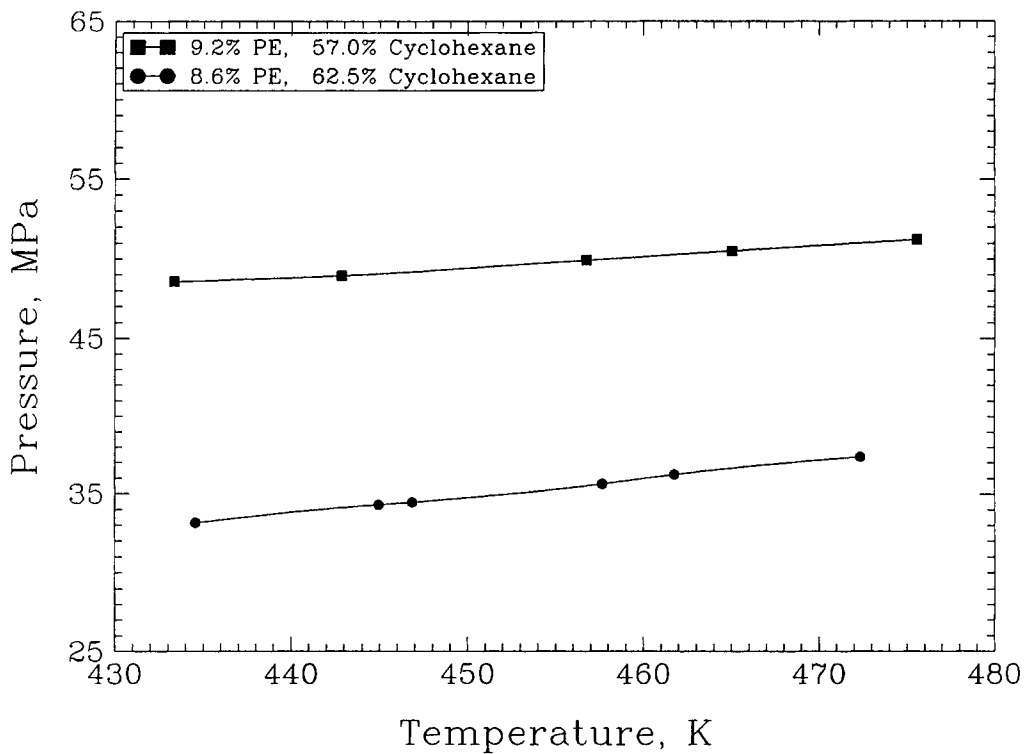


Figure 5 Demixing pressures for 9% by weight polyethylene solutions in the carbon dioxide-cyclohexane binary solvents. (Cyclohexane contents refer to their wt % amounts in the binary solvent, not the solution.)

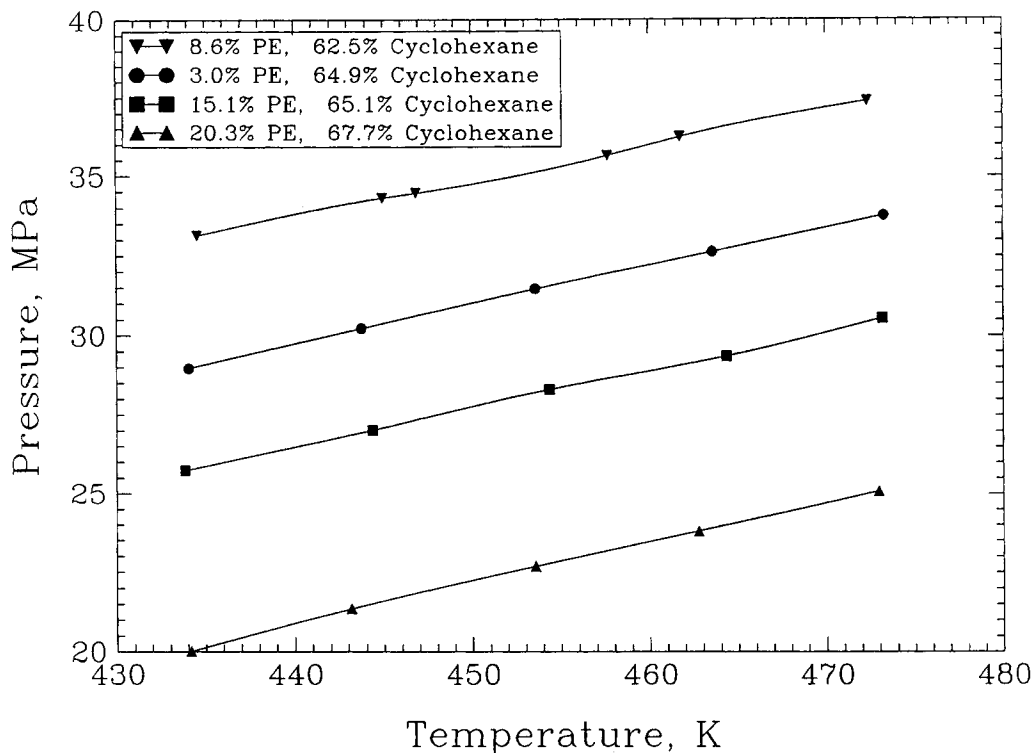


Figure 6 Dependence of demixing pressures on polymer concentration. (Polymer concentrations in the solutions are in wt %; cyclohexane amounts represent the wt % amounts in the binary solvent, not the solution.)

concentrations for polydisperse samples would not correspond to the maxima. Because of the strong dependence of demixing pressure on cyclohexane content (see Figs. 4 and 5), the P - T curve for the 8.6% solution in Figure 6 will shift to lower pressures if the cyclohexane content were increased to 65% level, and it is likely that in such a solvent the maximum in the pressure-composition (P - X) diagram will occur at polymer concentrations less than 3%. No attempts were however made to generate complete P - X diagrams at this time for any of these solvent compositions.

Solubility in Carbon Dioxide-Toluene Binary Mixtures

Figure 7(a) shows the demixing pressures for 3% polymer concentration in the binary solvent containing 50% toluene. The behavior is quite different than that for the carbon dioxide-cyclohexane case (Fig. 4). Here $(dP/dT)_c$ is negative and the demixing pressures decrease with increasing temperature. At a given pressure, one-phase regions are now entered with an increase in temperature. This is typical of the UCST behavior.

As shown in Figure 7(b), with an increase in the toluene content of the solvent, at 53.3%, demixing pressures are observed to display a decrease up to a certain temperature and then start to increase. At even higher toluene contents (at 56% by weight), $(dP/dT)_c$ becomes positive and the demixing pressures increase with increasing temperature [Fig. 7(c)]. Thus, depending on the toluene level, the behavior of the solution is observed to change from that of UCST to LCST.

A similar toluene-dependent changeover from UCST to LCST was also observed at higher polymer concentrations (up to 12% by weight that were investigated). For these solutions also the crossover was observed to be complete at a toluene content of about 56% by weight in the binary solvent.

Figure 8 is a comparative plot showing the demixing pressures for different polymer concentrations and toluene contents. A full range of polymer concentrations at a fixed solvent composition has not been carried out in this system. Nonetheless, the figure illustrates that, as in the case of cyclohexane, increasing the toluene content of the solvent decreases the demixing pressures. For a given toluene content, demixing pressures increase with in-

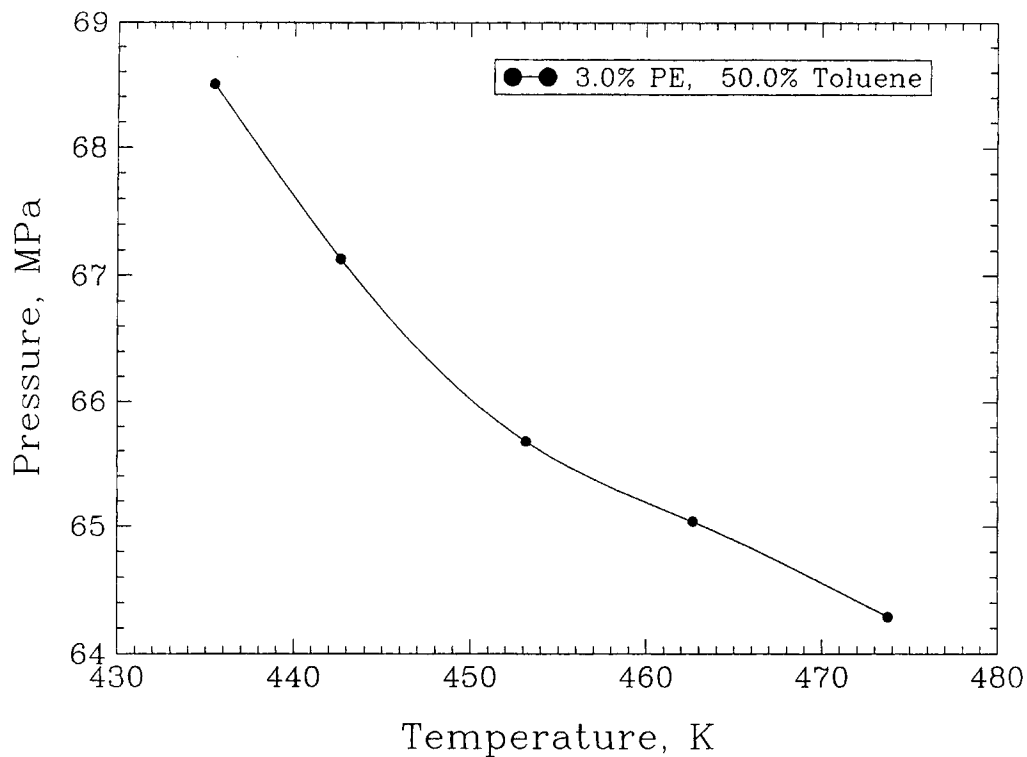


Figure 7a Demixing pressures for 3% by weight polyethylene solution in carbon dioxide-toluene binary solvent. Toluene content of the binary solvent is 50.0% by weight.

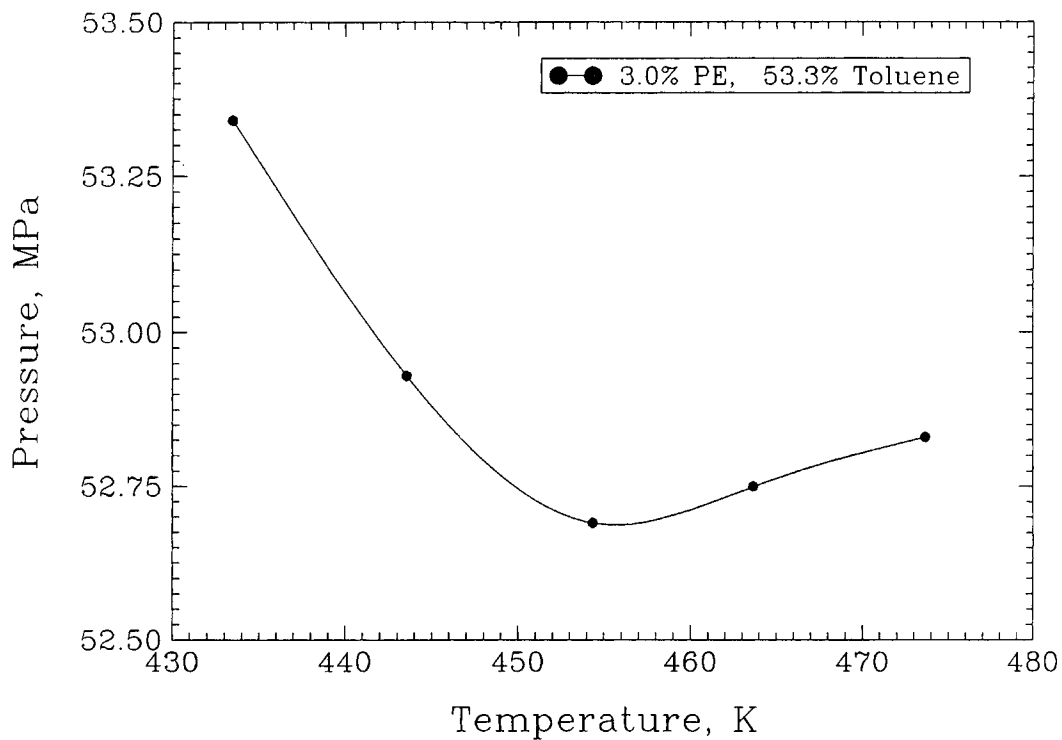


Figure 7b Demixing pressures for 3% by wt polyethylene solution in carbon dioxide-toluene binary solvent. Toluene content of the binary solvent is 53.3% by weight.

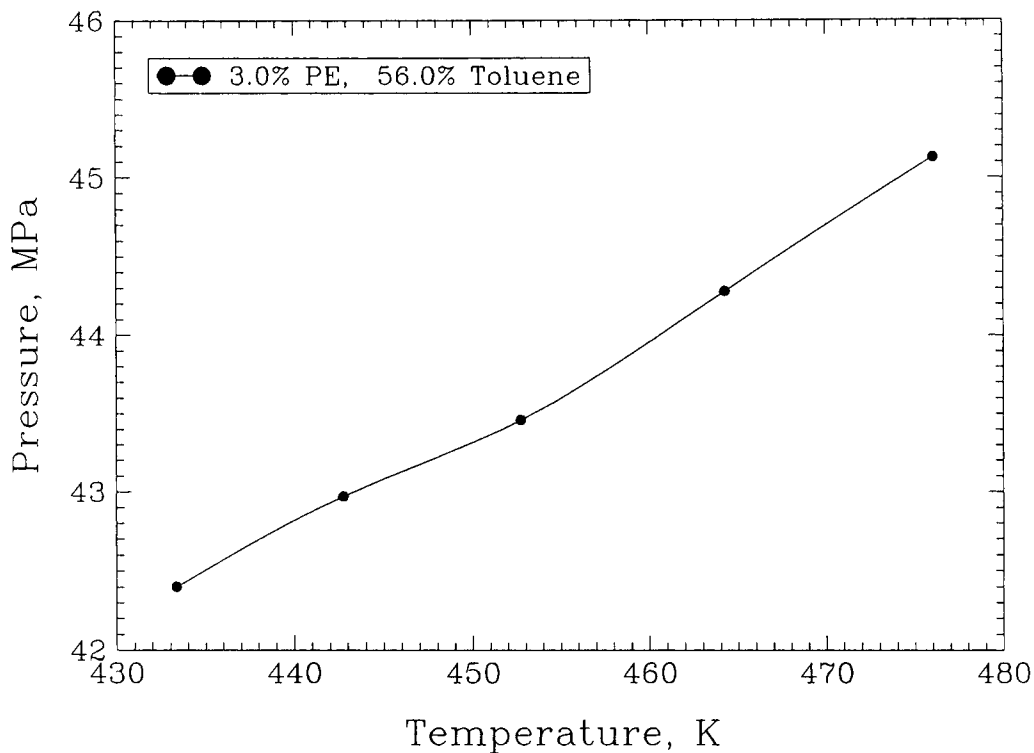


Figure 7c Demixing pressures for 3% by weight polyethylene solution in carbon dioxide-toluene binary solvent. Toluene content of the binary solvent is 56.0% by weight.

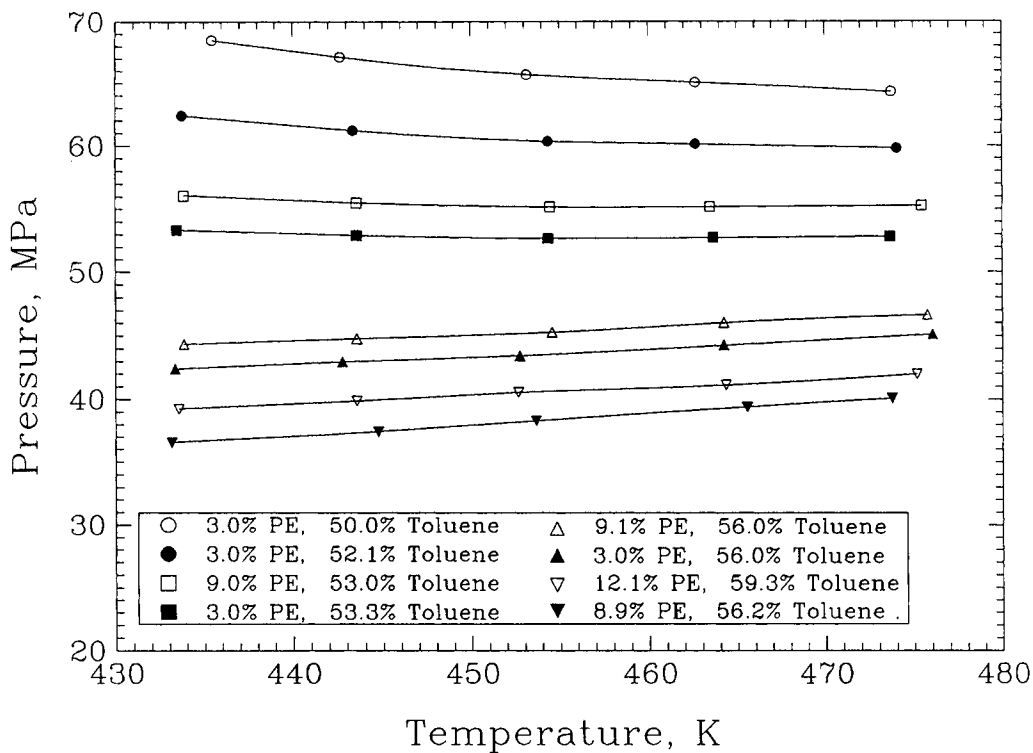


Figure 8 Dependence of demixing pressures on polymer concentration and solvent composition. (Polymer concentrations in the solutions are in wt %; toluene amounts refer to their wt % amounts in the binary solvent, not the solution.)

creasing polymer content in the solution. Even though the scale is much compressed, the change from UCST- to LCST-type behavior with the increasing amount of toluene in the solvent is readily noted.

Solubility in Carbon Dioxide–Pentane Binary Mixtures

In carbon dioxide–pentane mixtures, solubility tests were conducted at 3 and 9% by weight polymer concentrations. Figures 9 and 10 show the demixing pressures. Here data on solubility in pure pentane are also included. In the presence of carbon dioxide, the demixing pressures are significantly increased, from about 10 MPa in pure pentane to about 70 MPa in the binary mixture with 63% by weight *n*-pentane. In a given solvent, demixing pressures are observed to be lower for the 9% polymer solutions. This is explicitly illustrated in Figure 11.

Examination of these figures show that similar to the carbon dioxide–toluene system, the solutions in carbon dioxide–pentane binary solvent show a shift from UCST- to LCST-type behavior with an increase in the hydrocarbon content of the solvent.

It is noted that at pentane levels less than 70% by weight, solutions show UCSTs, at higher pentane contents behavior is that of LCST. That the behavior in pure pentane is that of LCST has already been well documented in the literature.^{7,23}

Comparison of Solubility in Different Carbon Dioxide–Hydrocarbon Binary Solvents

It is shown that the required amount of hydrocarbon is about 50% by weight for cyclohexane and toluene and is about 60% for pentane if complete dissolution of the polyethylene sample is to be achieved at pressures below 70 MPa. This can be linked to the fact that, for polyethylene, pentane is a much poorer solvent than toluene or cyclohexane.

For a given polymer concentration, the magnitude of the demixing pressures at comparable toluene or cyclohexane contents are quite similar. But much higher pressures are needed when the hydrocarbon is pentane. This is further illustrated in Figure 12, which compares the demixing pressures for 9% polymer solutions in solvents with comparable hydrocarbon contents (62.5% cyclohexane, 59.2% toluene, 63% pentane). These results again reflect the

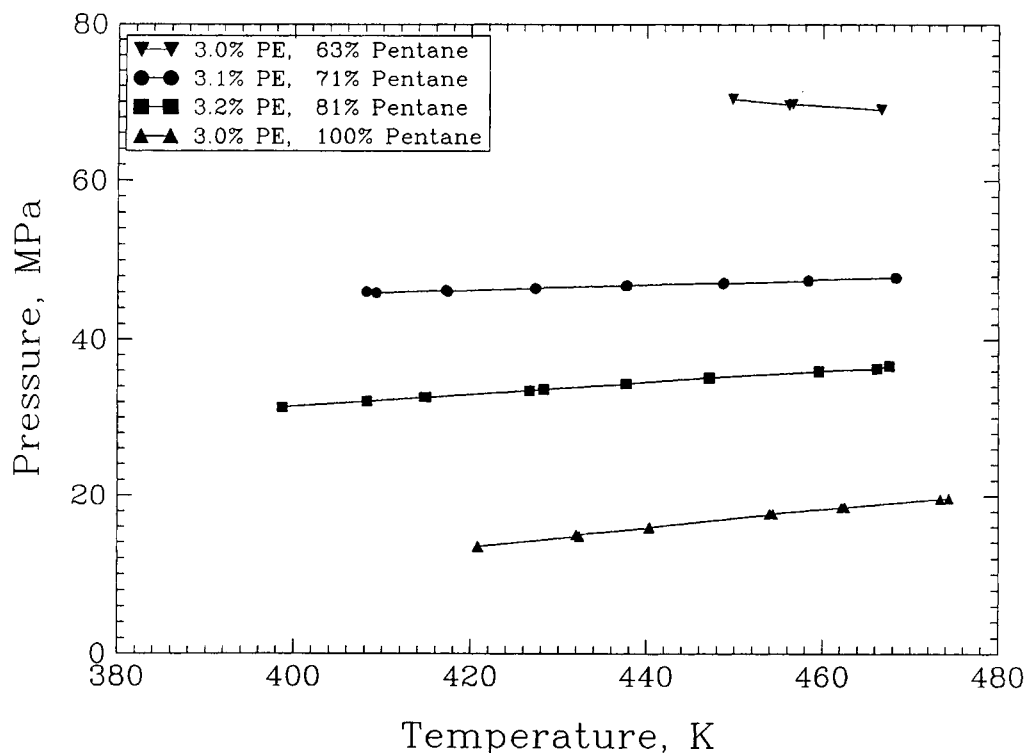


Figure 9 Demixing pressures for 3% by weight polyethylene solutions in carbon dioxide–pentane binary solvents. (Pentane contents refer to their wt % amounts in the binary solvent, not the solution.)

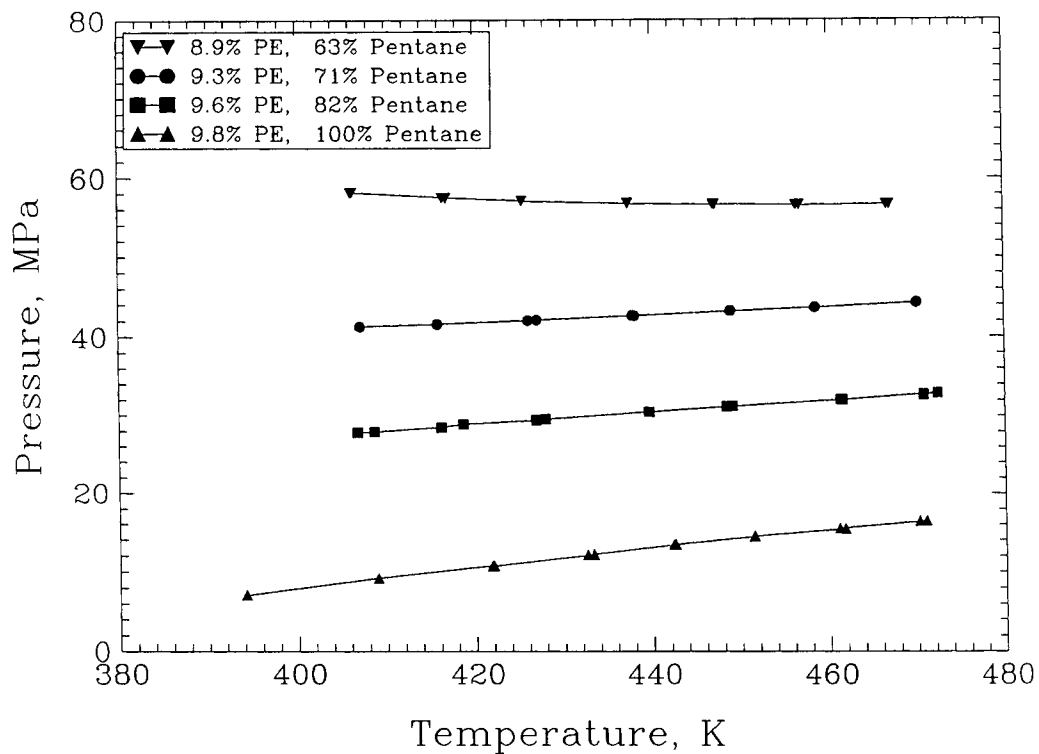


Figure 10 Demixing pressures for 9% by weight polyethylene solutions in carbon dioxide-pentane binary solvents. (Pentane contents refer to their wt % amounts in the binary solvent, not the solution.)

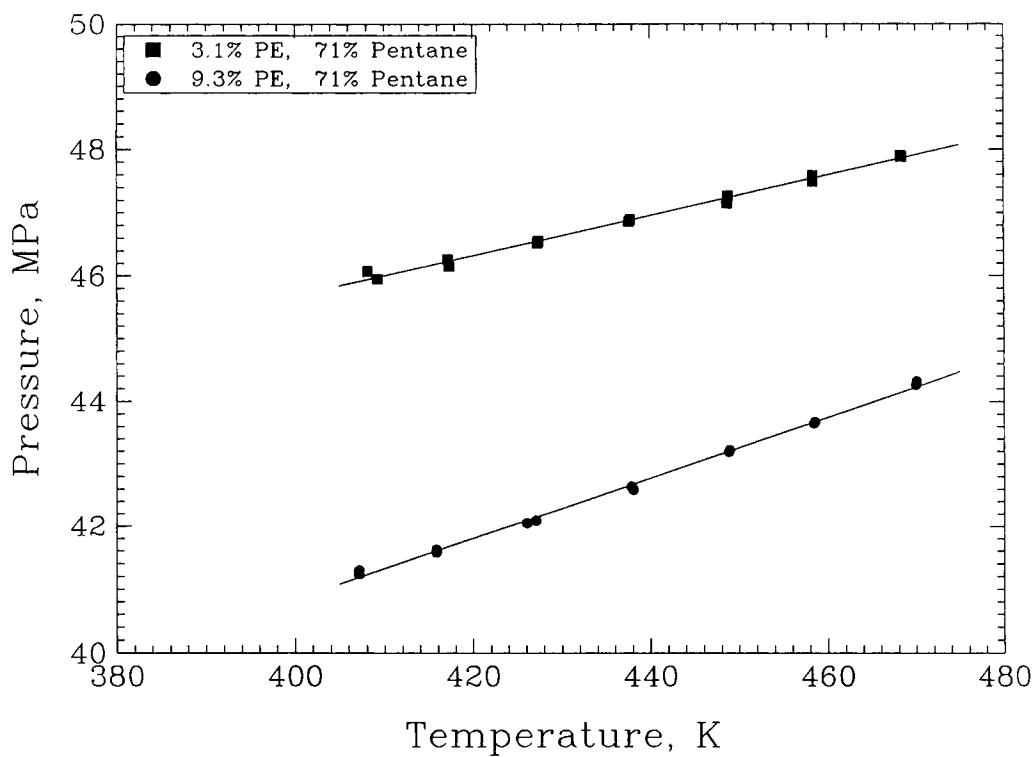


Figure 11 Dependence of demixing pressures on the polymer concentration. (Polymer concentration in the solution is given as wt %; pentane amount is the wt % amount in the binary solvent, not the solution.)

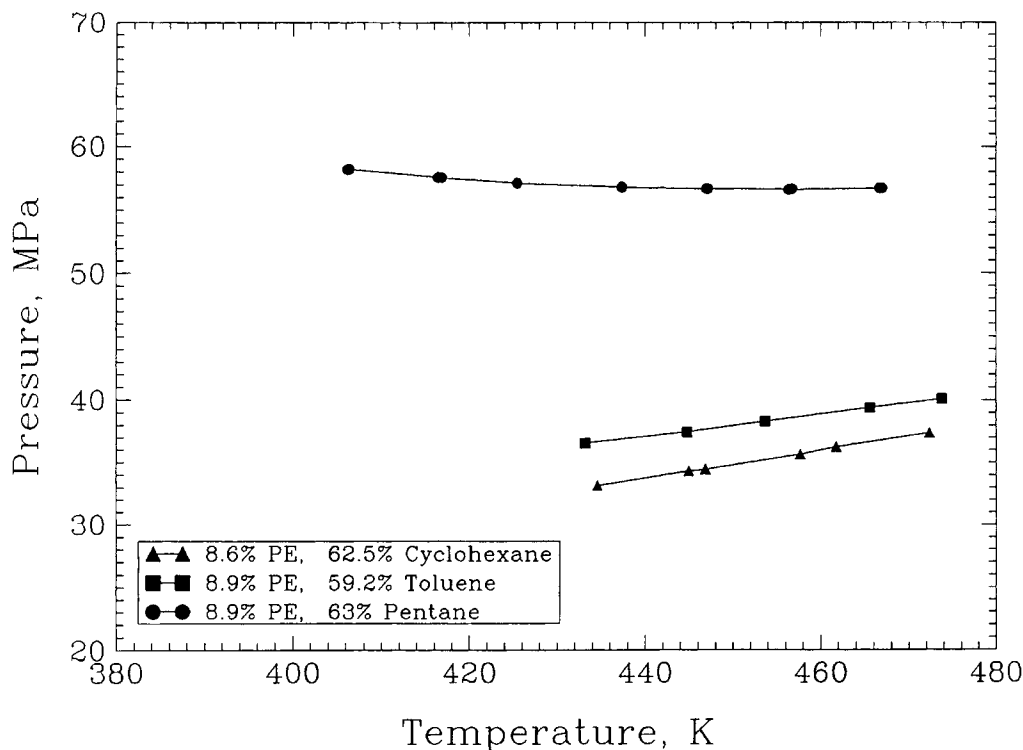


Figure 12 Dependence of the demixing pressures of polyethylene solutions on the type of hydrocarbon in the carbon dioxide–hydrocarbon binary solvent. (Hydrocarbon amounts refer to their wt % amounts in the binary solvent, not the solution).

poorer nature of pentane as a solvent. At a given hydrocarbon level in the binary, solvent quality decreases in going from cyclohexane to toluene and to pentane.

An interesting observation is the crossover from UCST to LCST for the solutions with increasing hydrocarbon content in the binary solvents carbon dioxide–toluene and carbon dioxide–pentane. Such a crossover is not observed in the carbon dioxide–cyclohexane system for the solvent compositions tested. Cyclohexane contents were all greater than 53%. It is possible that the crossover might have been completed at a cyclohexane content less than 53.3%. Regardless, carbon dioxide–toluene and carbon dioxide–pentane mixtures behave as poorer solvents for polyethylene than carbon dioxide–cyclohexane mixtures.

FURTHER DISCUSSION

Since the discovery of LCST phenomena in non-polar polymer–solvent systems in 1960,³¹ the question of LCST and UCST in polymer solutions have been the subject of a large number of investigations.^{7,21,23–26,31–44}

Basic thermodynamic requirement for mixing is that the free energy of mixing ΔG_m must be negative. Since

$$\Delta G_m = \Delta H_m - T \Delta S_m$$

mixing will be favored when the enthalpy of mixing is negative, or the entropy of mixing is sufficiently positive.

An increase in solubility with an increase in temperature is associated with an endothermic heat of mixing, and therefore UCST is linked to an unfavorable energy effect, that is, a positive, rather than a negative ΔH_m . When temperature is lowered, the heat term may become larger than the entropy term and cause phase separation.

Observation of UCST may be indicative of the dissimilar nature of the polymer and the solvent. Normally, the mutual solubility of a nonpolar polymer with a polar or other poor solvents increases with increasing temperature until complete miscibility is reached at an upper critical solution temperature. UCST is not normally observed in chemically similar systems, such as polystyrene–benzene solutions.

The observation that solutions of polyethylene in carbon dioxide–toluene and carbon dioxide–pentane binary solvents display UCST at low hydrocarbon contents are suggestive of an unfavorable heat of mixing and point to the increased dissimilarity between the polymer and the solvent mixture as the hydrocarbon fraction in the solvent is lowered. As will be discussed later this is also linked to the lowering of the critical temperature upon lowering the hydrocarbon content in these binary solvent mixtures. It is likely that similar behavior can also be observed in the carbon dioxide–cyclohexane system if the critical temperature were sufficiently reduced by further lowering the cyclohexane content of the mixture.

In contrast to UCST, in systems displaying LCST, the mutual solubility increases with decreasing temperature. Such behavior is observed in systems where the polymer and the solvent are either both highly polar or nonpolar. When highly polar systems are involved, such as the aqueous solutions of polyethylene oxide, LCST is usually below the boiling temperature of the solvent. In contrast, the LCST in nonpolar systems, such as solutions of polystyrene in benzene, or polyethylene in *n*-alkanes, is usually found at temperatures higher than the boiling temperature of the solvent. The phenomenon occurs at temperatures approaching the solvent critical temperature.

Thermodynamically, a decrease in solubility with a rise in temperature is indicative of a negative (exothermic) heat of mixing. The eventual phase separation at high enough temperatures, i.e., the LCST, therefore must involve an unfavorable (negative) entropy effect.

In nonpolar systems, as the system temperature approaches the critical temperature of the solvent, the solvent molecules undergo an expansion in the direction of reducing the distinction between liquid and gas, which would eventually disappear at the critical point. The polymer molecule, however, being far removed from its critical point, does not undergo such an expansion. Instead, the polymer molecules confine the solvent molecules to a more rigid matrix, leading to a decreased entropy of mixing, and consequently phase separation.

The unfavorable entropy effect thus arises from the differences in the expansivity (or free volume) of the polymer and the solvent.⁴⁴ Due to the connectivity of the polymer segments, the volume of solution is closer to the volume of the polymer than the solvent. That is, in the dissolution process, the solvent which is initially in a highly expanded state, is forced to lose a significant portion of its free

volume. It is noted that the solution process is in a way a condensation process,³⁷ which is exothermic and involves a decrease in entropy. As temperature increases, the difference in free volume also increases and when the LCST is reached, entropy effect dominates the heat effect and phase separation occurs. On the other hand, the difference in free volume between polymer and solvent will decrease with increasing pressure, and solubility will be increased. This is in fact experimentally observed.

The free volume theory of liquids⁴⁴ predicts that all systems will have a LCST, whereas unfavorable positive heats of mixing at low temperature can lead to UCST. Nonpolar polymer–solvent systems can display both LCST and UCST. This is in fact what is observed in the present study.

Table III shows the critical temperatures of the binary solvent mixtures corresponding to the demixing data shown in Figures 4–12. As shown in Figures 2 and 3, the critical behavior of carbon dioxide–cyclohexane and carbon dioxide–toluene show great similarities. In carbon dioxide–pentane, mixture critical values are lower than the critical temperatures and pressures for the other binary mixtures.

For binary solvent compositions in which critical temperatures are high, demixing temperatures are observed below T_c and the solutions all show LCST behavior. This is in line with the free volume argument and the large difference in expansivity that the solution would experience as the temperature is raised toward the critical temperature, leading to phase separation upon heating. Phase separations in these systems appear to take place at temperatures 15 to 50°C below the respective critical temperatures. Literature on other polymer systems reports that polymers of low molecular weight may undergo phase separation within 20 or 30°C of the solvent's gas–liquid critical temperature, whereas polymers of high molecular weight (greater than 10^6) separate at temperatures as much as 120 below the gas–liquid critical temperature.³³

Table III also shows that as the critical temperature of the solvent is lowered, demixing behavior starts to shift from LCST to finally UCST, with demixing temperatures being observed at temperatures greater than the critical temperature of the solvent mixture.

CONCLUSIONS

It is shown that the solubility of polyethylene in carbon dioxide–hydrocarbon binary mixtures depends on the hydrocarbon content of the binary sol-

Table III Comparison of Phase Separation Temperatures with the Critical Temperatures of Carbon Dioxide–Hydrocarbon Binary Solvents

Wt % Hydrocarbon	T_c (K)	Temperature Range of Demixing Data	Comment	LCST/UCST
<i>Cyclohexane</i>				
53.3	457	435–475	$T \geq T_c$	LCST
57.0	468	435–475	$T < T_c$	LCST
62.5	482	435–475	$T < T_c$	LCST
64.9	489	435–475	$T < T_c$	LCST
65.1	489	435–475	$T < T_c$	LCST
67.7	495	435–475	$T < T_c$	LCST
<i>Toluene</i>				
50.0	450	435–475	$T \geq T_c$	UCST
53.3	465	435–475	$T \leq T_c$	Transition
56	477	435–475	$T < T_c$	LCST
59.1	489	435–475	$T < T_c$	LCST
<i>Pentane</i>				
62	422	440–470	$T > T_c$	UCST
71	436	390–470	$T \leq T_c$	Transition
81	450	390–470	$T < T_c$	LCST
100	469	420–475	$T < T_c$	LCST

vent. Solubility increases with increasing hydrocarbon content. At a given hydrocarbon content, dissolving power decreases in going from cyclohexane to toluene and to pentane.

Depending on the solvent composition and the critical temperature of the binary solvent, solutions display either UCST- and LCST-type behavior.

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