

AD-A154 514

POLYMER SOLUTION-SUPERCRITICAL FLUID BEHAVIOR(U) NOTRE
DAME UNIV IN DEPT OF CHEMICAL ENGINEERING
A K MCCLELLAN ET AL. 10 APR 85 TR-2 N00014-83-K-0613

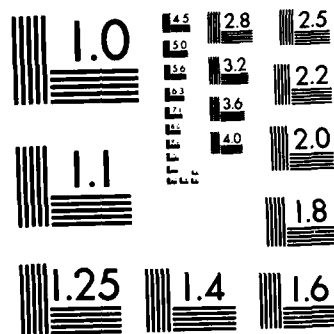
1/1

UNCLASSIFIED

F/G 7/4

NL





MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

AD-A154 514

OFFICE OF NAVAL RESEARCH

Contract N00014-83-K-0613

Task No. NR 625-841

Technical Report No. 2

"Polymer Solution-Supercritical Fluid Phase Behavior"

by

Alan K. McClellan, Evan G. Bauman, and Mark A. McHugh

Prepared for Publication

in the

Symposium Proceedings on Supercritical Fluid Technology, San Francisco,

CA., Elsevier Science Publishers

University of Notre Dame
Department of Chemical Engineering
Notre Dame, IN 46556
April 10, 1985

Reproduction in whole, or in part, is permitted for any purpose of the
United States Government

* This document has been approved for public release and sale; its
distribution is unlimited

Accession For	
NTIS GRA&I	☒
DTIC TAB	☐
Unannounced	☐
Justification	
By _____	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A/	

DTIC
ELECTE

JUN 5 1985

85

5

08

050

DTIC FILE COPY

Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) Mark A. McHugh Dept. of Chemical Engineering Univ. of Notre Dame, Notre Dame, IN 46556		2a. REPORT SECURITY CLASSIFICATION Unclassified	
		2b. GROUP	
3. REPORT TITLE POLYMER SOLUTION-SUPERCRITICAL FLUID PHASE BEHAVIOR			
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Technical Report, Interim July 1, 1984 - June 30, 1985			
5. AUTHOR(S) (First name, middle initial, last name) Alan K. McClellan, Evan G. Bauman, Mark A. McHugh			
6. REPORT DATE 04/05/85		7a. TOTAL NO. OF PAGES 20	7b. NO. OF REFS 18
8a. CONTRACT OR GRANT NO. N00014-83-K-0613		9a. ORIGINATOR'S REPORT NUMBER(S) TR-2	
b. PROJECT NO.			
c.		9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
d.			
10. DISTRIBUTION STATEMENT Distribution of this document is unlimited.			
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY Office of Naval Research, 612A:BAR Department of the Navy, 800N. Quincy Street Arlington, Va. 22217	
13. ABSTRACT Experimental pressure - temperature (P-T) data are presented for the polystyrene - toluene - carbon dioxide system and the polystyrene - toluene - ethane system. The P-T phase diagrams for these systems exhibit characteristics which are similar to the phase diagrams of simple binary solutions. The addition of supercritical carbon dioxide and supercritical ethane to the polystyrene - toluene solution shifts the lower critical solution temperature curve to lower temperatures. Polymer - organic solvent - supercritical fluid additive phase behavior is interpreted in terms of Patterson's corresponding states model. Representative calculations using this model are shown for the poly(ethylene-co-propylene) - hexane - supercritical ethane system. <i>Originator Supplied keywords include:</i>			

14	KEY WORDS	LINK A		LINK B		LINK C	
		ROLE	WT	ROLE	WT	ROLE	WT
	continued Thermodynamic, Polymers, Lower critical solution temperature, Supercritical fluid.						

POLYMER SOLUTION-SUPERCRITICAL FLUID PHASE BEHAVIOR

A. K. McCLELLAN, E. G. BAUMAN, AND M. A. MCHUGH

Department of Chemical Engineering, University of Notre Dame
Notre Dame, Indiana 46556

ABSTRACT

Experimental pressure - temperature (P-T) data are presented for the polystyrene - toluene - carbon dioxide system and the polystyrene - toluene - ethane system. The P-T phase diagrams for these systems exhibit characteristics which are similar to the phase diagrams of simple binary solutions. The addition of supercritical carbon dioxide and supercritical ethane to the polystyrene - toluene solution shifts the lower critical solution temperature curve to lower temperatures.

Polymer - organic solvent - supercritical fluid additive phase behavior is interpreted in terms of Patterson's corresponding states model. Representative calculations using this model are shown for the poly(ethylene-co-propylene) - hexane - supercritical ethane system.

INTRODUCTION

Separating solvent from polymer is one of the final processing stages which occurs during a solution polymerization process. Typically, the solvent is steam stripped from the polymer solution. However, steam stripping is an energy intensive process and, as such, is very costly. It is therefore desirable to investigate other separation techniques.

Separating the solvent from a polymer solution is also accomplished by forcing the single phase, miscible polymer solution to split into two equilibrium phases: a polymer-rich phase and a solvent-rich phase. It is well known that miscible polymer-solvent solutions exhibit liquid-liquid immiscibility as the solution temperature approaches the critical temperature of the solvent (1). This liquid-liquid immiscibility occurs at the lower critical solution temperature (LCST). The LCST is a function of the chemical nature of the solvent, the polymer molecular weight, and the

critical properties of the solvent. For instance, Bardin and Patterson (2) report an LCST to solvent critical temperature (T_c) ratio as low as 0.73 for the polyisobutylene - n-pentane system and as high as 0.98 for the polyisobutylene - cyclooctane system. In general, a polymer with a molecular weight on the order of 10,000 exhibits an LCST which is 20-30 K lower than the solvent T_c while a polymer with a molecular weight of 1,000,000 can have an LCST nearly 100 K below the solvent T_c .

The phase behavior for several polymer - solvent systems are reported in the literature. Freeman and Rowlinson (1) discuss the LCST behavior of hydrocarbon polymers with short chain alkane solvents and their isomers. Baker, et al. (3,4) describe the LCST behavior of polyisobutylene - n-pentane and polyisobutylene - isopentane mixtures. The phase behavior of polystyrene - solvent mixtures is reported by Zeman and Patterson (5), Allen and Baker (6), Saeki, et al. (7), and Cowie and McEwen (8). In each case, the LCST is measured at the vapor pressure of the mixture at various concentrations of polymer. To realize the full potential of this technique it is necessary to understand the phase behavior which can be exhibited by polymer - solvent mixtures at high pressures.

A schematic pressure temperature (P-T) diagram for a typical polymer - solvent system is shown in Figure 1a. C_1 is the critical point of the pure solvent and C_2 is the critical point of the polymer, which in this case is probably fictitious, since the polymer will degrade before it exhibits critical phenomena. The dashed lines are the critical mixture curves. The critical mixture curve which starts at C_2 intersects a liquid - liquid - vapor (LLV) region at the LCST and the branch of the critical mixture curve starting at C_1 ends at an upper critical end point (UCEP). At temperatures below the critical temperature of the solvent a second LLV region appears which ends in a UCEP. The upper critical solution temperature (UCST) curve, in Figure 1a, represents

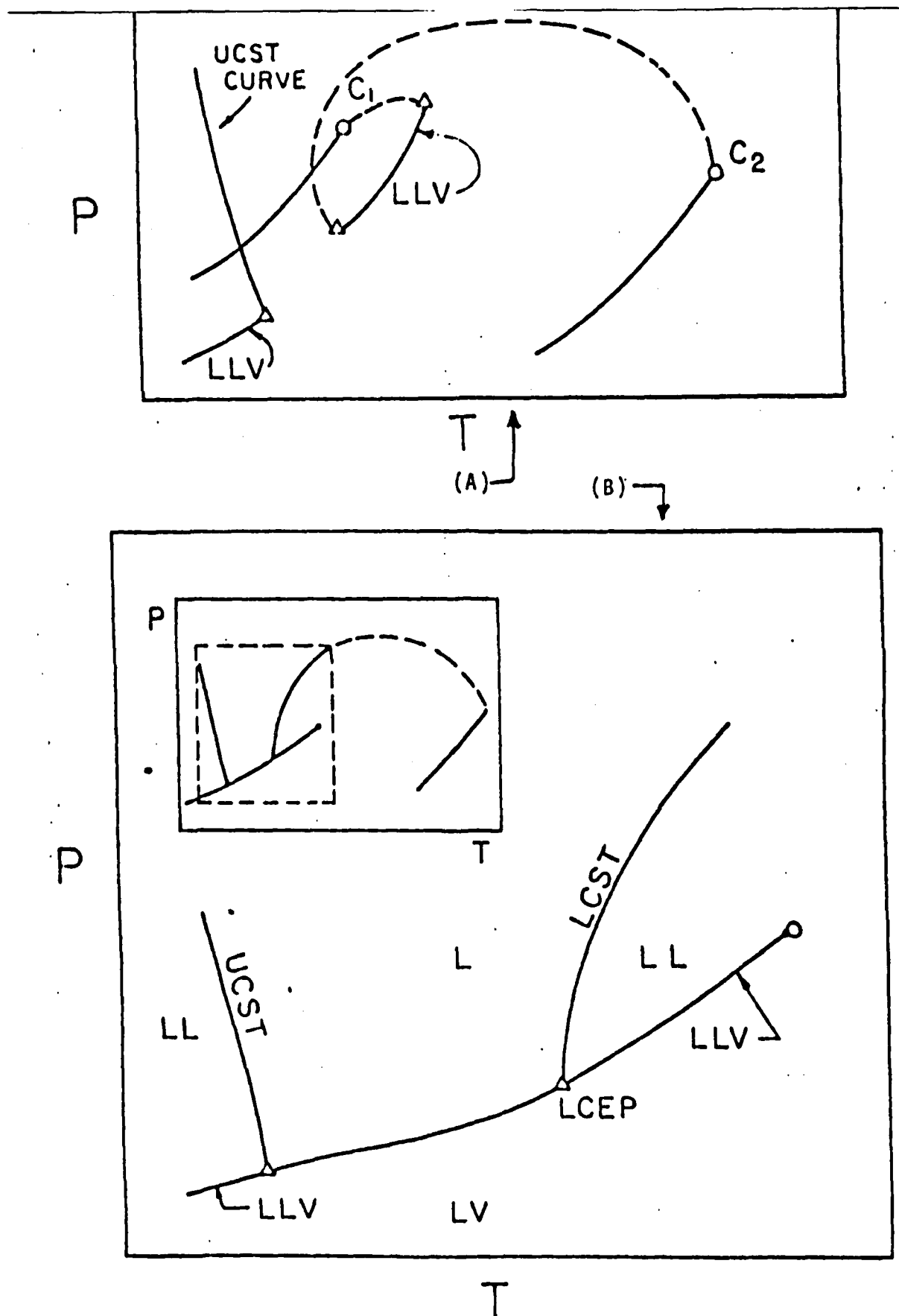


Figure 1. Schematic pressure-temperature diagram for polymer-solvent mixtures.

the effect of pressure on the transition from two liquid phases to one liquid phase as the system temperature is isobarically increased. Baker, et al. (3) show that the LLV curve of a polymer - solvent mixture is indistinguishable from the vapor pressure curve of the pure solvent. The section of Figure 1a close to the critical point of the pure solvent is enlarged and shown in Figure 1b with this simplification. Although the intersection of the critical mixture curve with the LLV curve, is by definition, the LCST for polymer - solvent systems, this intersection is commonly known as the lower critical end point (LCEP) (ie., at the LCEP two liquids become critically identical in the presence of a vapor phase). The critical mixture curve in the region of the critical point of the pure solvent is referred to as the LCST curve since the phase transition which occurs along this curve exhibits the characteristics of a liquid - liquid to fluid transition rather than a liquid - vapor to fluid transition.

Although inducing a polymer-solvent phase split offers certain advantages as compared to steam stripping, it is necessary to heat the polymer solution to temperatures near the solvent critical temperature which, for good polymer solvents, can be very high. To avoid thermally degrading the polymer at these high temperatures inhibitors are added to the solution. Alternatively, Irani, et al. (11) show that the LCST can be shifted to moderate temperatures by introducing a light, supercritical fluid (SCF) additive to the polymer solution. The overall effect of the SCF additive on the phase behavior is to lower the LCST curve without affecting the phase diagram as illustrated in Figure 2.

Experimental data are presented in this paper on the P-T behavior of the polystyrene-toluene-SCF additive system where ethane and carbon dioxide are used as the SCF additive. The experimental procedure for obtaining this data is outlined. The corresponding states model of Patterson is used to interpret the experimental data. Representative calculations using this model are shown for the poly(ethylene-co-propylene) - hexane - supercritical ethane

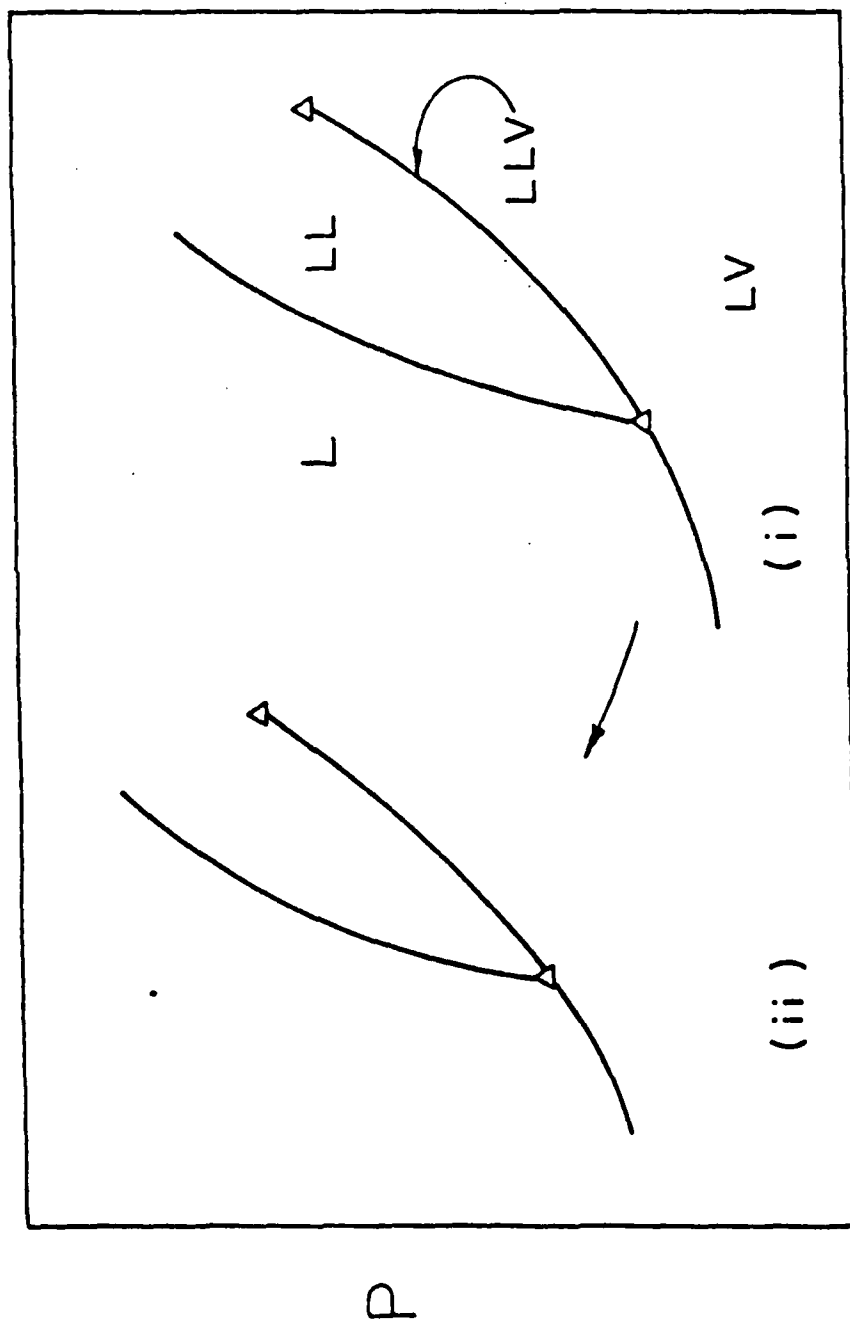


Figure 2. The effect of SCF additive on the polymer-solvent phase behavior.

system.

EXPERIMENTAL

The experimental apparatus and procedure used in this study (see Figure 3) are described elsewhere (13), and therefore, are only briefly described here. A measured amount of polymer solution is first loaded into a high pressure, variable-volume, equilibrium view cell. The concentration of the polymer in the organic solvent is normally maintained at approximately 5 wt% to ensure that the cloud point curve obtained is very close to the actual LCST curve (9,12). A known amount of SCF additive is then added to the equilibrium cell.

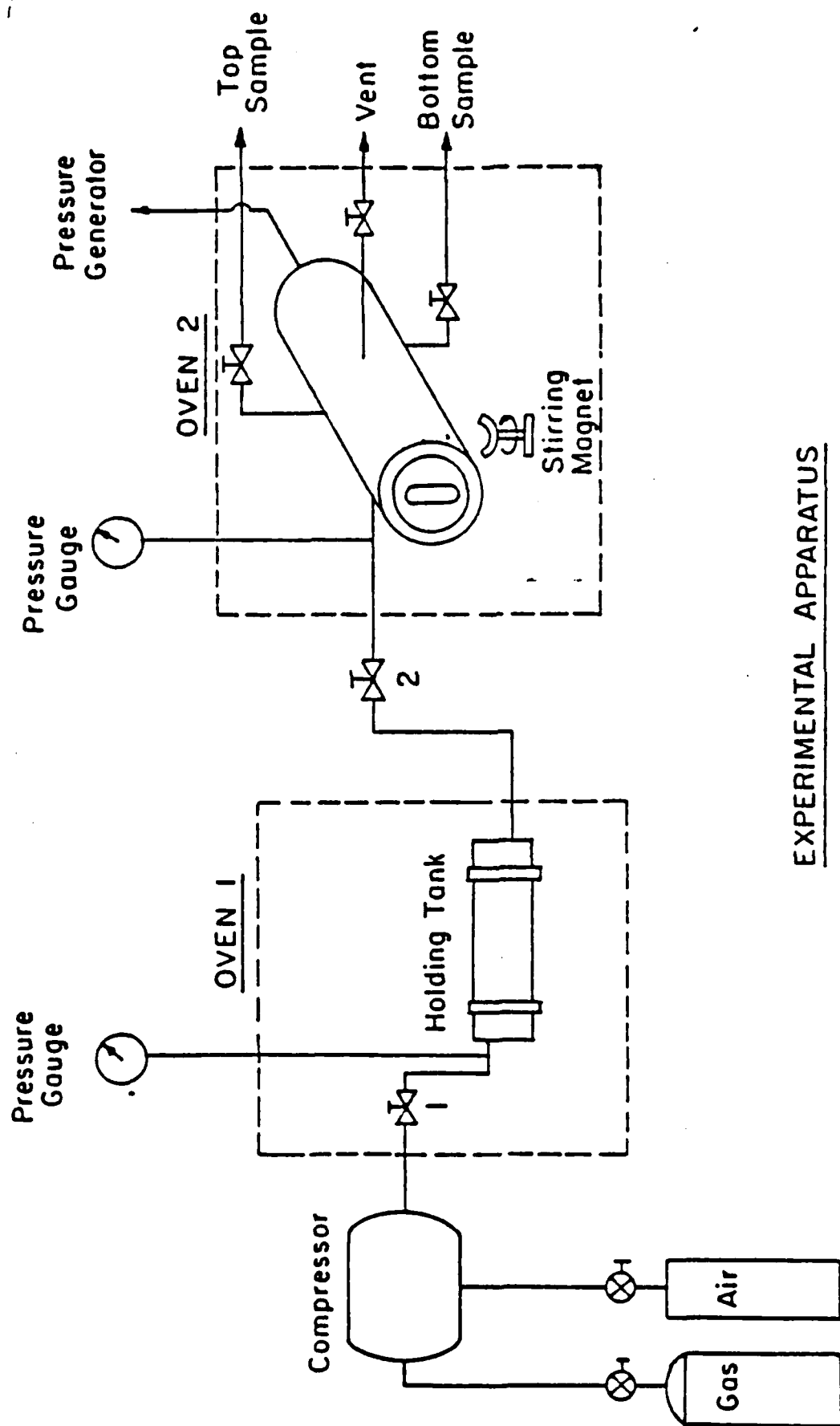
The high pressure, variable-volume, equilibrium view cell is designed to operate at 35 MPa and 530 K. The cell contents, illuminated by a fiber light pipe, are viewed through a quartz window, which is secured by a cell end-cap. The contents of the cell are mixed with a stirring bar, activated by a magnet, which is located below the cell. The volume of the cell is varied by a movable piston, hence, the phase boundaries are visually obtained at a fixed overall composition.

MATERIALS

The properties of the polystyrene donated by the Dow Chemical Company are listed in Table I. The toluene, reagent grade, is supplied by the Sargent-Welch Corp. The ethane, CP grade 99.5% minimum purity, and the carbon dioxide, bone-dry grade 99.8% minimum purity, are supplied by the Linde Company. These components are used without further purification.

RESULTS AND DISCUSSION

The pressure - temperature (P-T) projection of various polystyrene-toluene-SCF transition curves are shown in Figures 4 through 7 for supercritical carbon dioxide and ethane. No attempt is made to locate the



EXPERIMENTAL APPARATUS

Figure 3. Schematic diagram of the experimental apparatus used in this study.

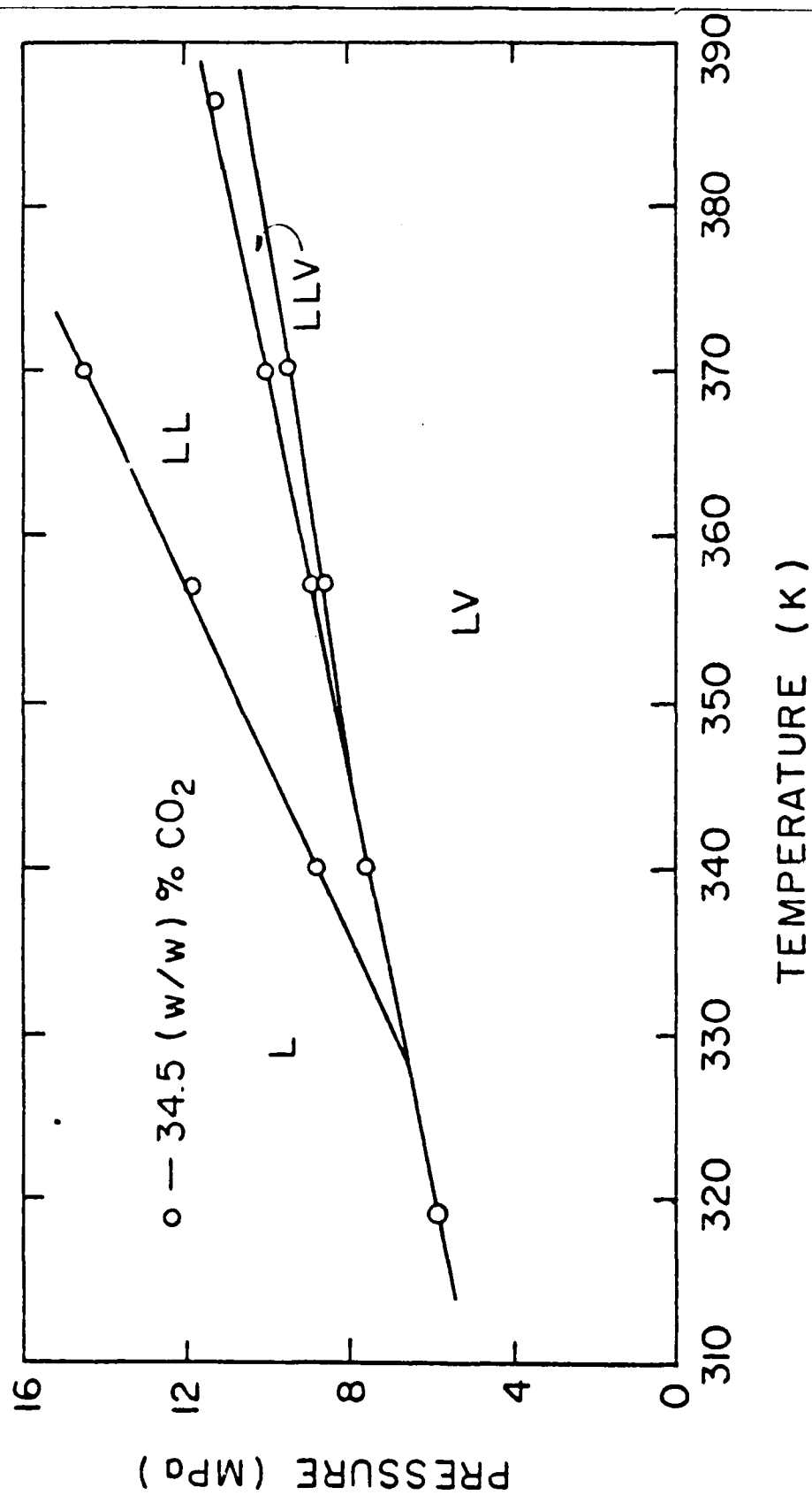


Figure 4. Pressure-temperature projection of the polystyrene-toluene-carbon dioxide system.

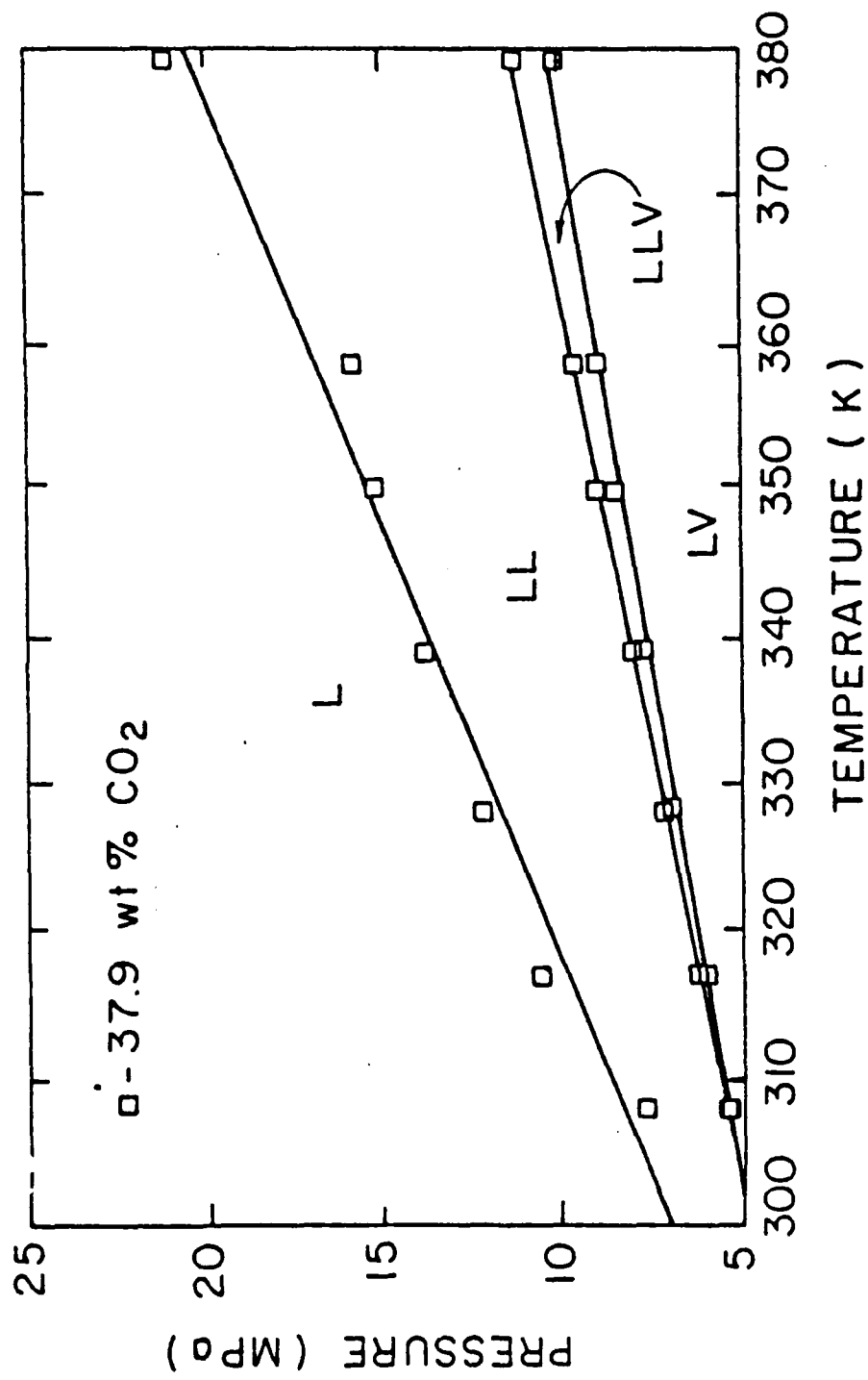


Figure 5. Pressure-temperature projection of the polystyrene-toluene-carbon dioxide system.

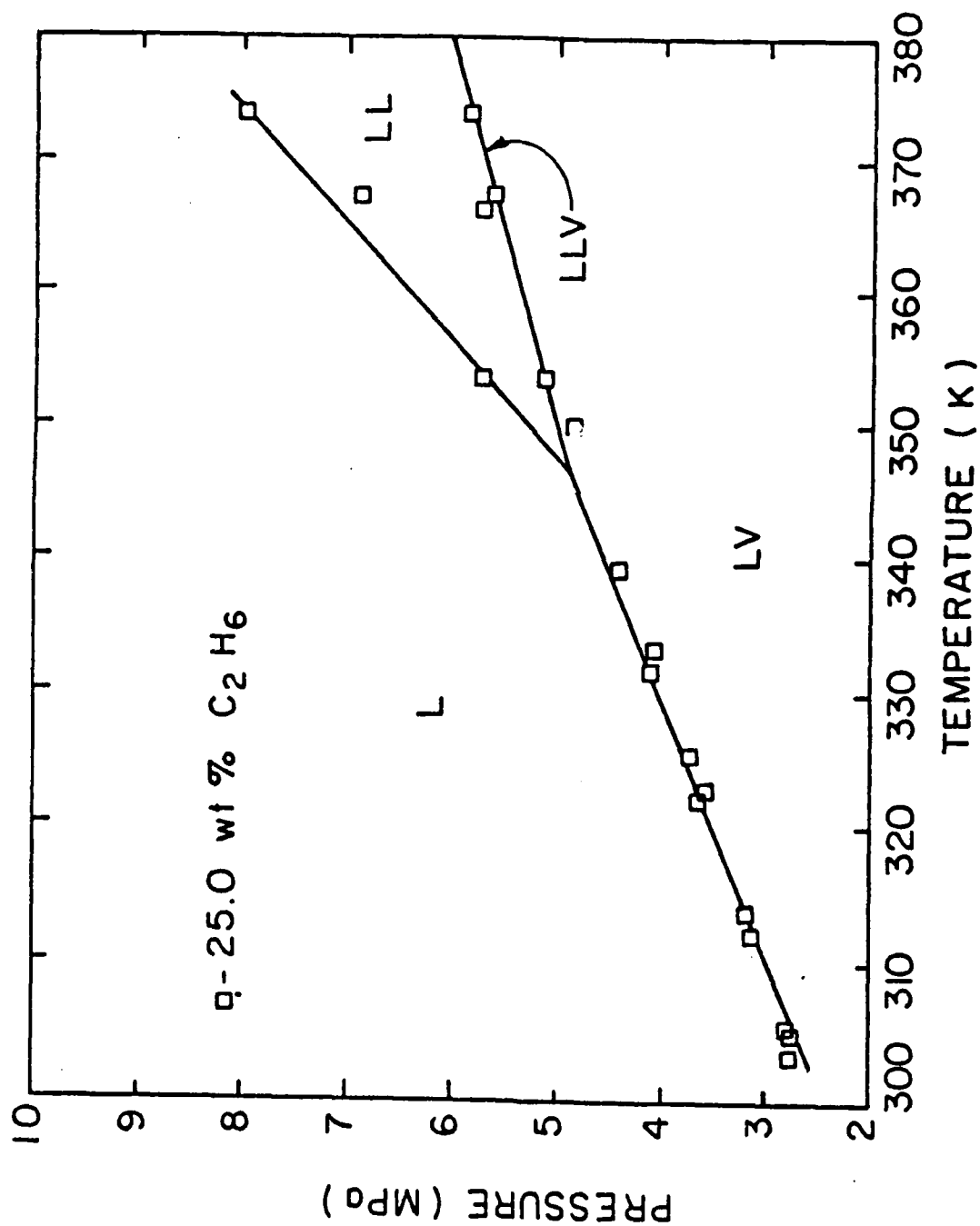


Figure 6. Pressure-temperature projection of the polystyrene-toluene-ethane system.

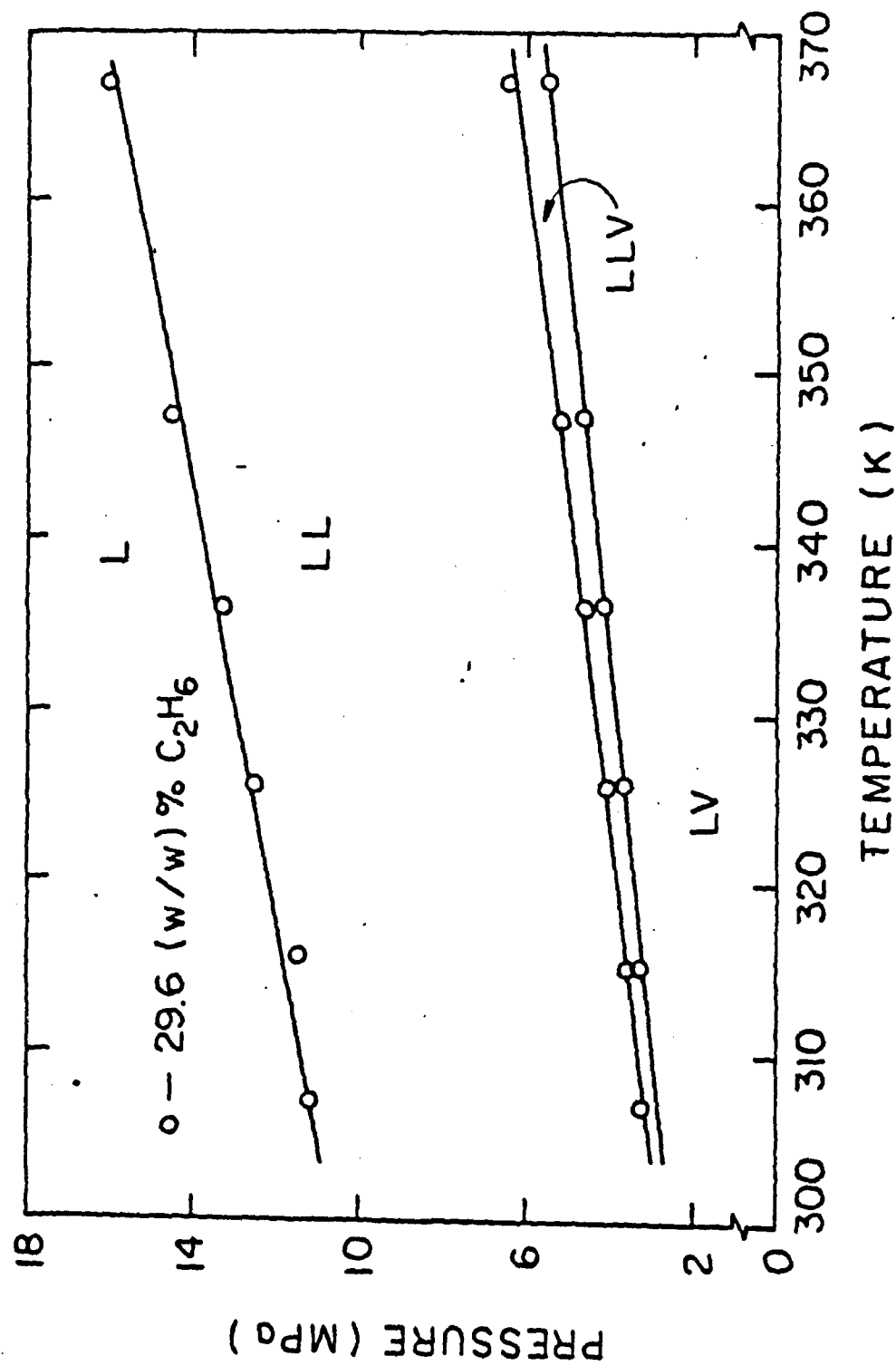


Figure 7. Pressure-temperature projection of the polystyrene-toluene-ethane system.

upper critical solution temperature curve for these systems.

Shown in Figure 4 are the experimental P-T data for the polystyrene - toluene - carbon dioxide system at 34.5 wt% carbon dioxide. The weight percent of carbon dioxide is based on the total weight of the solution. Without any carbon dioxide added to the polystyrene-toluene solution, the phase border curves depicted in this figure are located approximately 220 K higher in temperature (14).

The polystyrene-toluene-carbon dioxide system at 37.9 wt% carbon dioxide is shown in Figure 5. The slope of the LCST curve in this figure has changed considerably from the 34.5 wt% system. The LCEP is not determined for this system, although if the LCST curve and the LLV curve are extrapolated to lower temperatures, the LCEP is approximately 45 K lower than the LCEP for the 34.5 wt% system.

Shown in Figures 6 and 7 are the P-T curves for the polystyrene - toluene - ethane systems for ethane loadings of 25.0 wt% and 29.6 wt%. For the 25 wt% ethane system the LCEP is approximately 347 K. The 29.6 wt% ethane system, shown in Figure 7, exhibits a critical mixture curve that is parallel to the LLV line. In this case, the LCST and the UCST curves have merged to form a single curve and, hence, the critical mixture curve never intersects the LLV curve.

It is interesting to note that Figures 4 through 7 all exhibit a region of LLV immiscibility. This immiscibility behavior is in contrast to the phase behavior exhibited by binary mixtures of small molecules where the LLV region is a single line in P-T space. The LLV regions in Figures 4 through 7 are a consequence of the multicomponent nature of the polymer.

The composition of the equilibrium phases in the liquid - liquid region of the polystyrene - toluene - 29.6 wt% ethane system at 311.1 K and 9.1 MPa is presented in Table 1. This compositional data shows that the polymer concentration increases from 5 wt% to 15 wt% in the polymer-rich phase. Further studies are in progress to expand on this data base and to determine

the molecular weight and the molecular weight distribution of the polymer in the equilibrium phases.

Table 1. Composition Analysis for Polystyrene (PS)- Toluene - Ethane (29.6 wt%) System.

	T = 311.1 K	
	P = 9.1 MPa	
	Light Phase	Heavy Phase
<u>Component</u>	<u>wt %</u>	<u>wt %</u>
PS	0.3	15.8
Toluene	73.9	64.3
Ethane	25.8	19.9

PS: $M_w = 239,000$

$M_n = 221,000$

$M_w/M_n = 1.08$

MODELLING

To model the phase behavior obtained in this study it is necessary to obtain a value of the Flory - Huggins free energy parameter

$$\chi_c = 1/2(1 + r^{-1/2})^2 \quad (1)$$

where

$$r = V_s^*/V_p^* \quad (2)$$

the superscript * represents a reduction parameter. Using the model of

Patterson and coworkers (15) the critical mixture curve for polymer solutions at low polymer concentrations are calculated with

$$x_c(P,T) = c(-v^2 U_s/T_s + 1/2 C_{p,s}(P_s, T_s) (\tau + P_s V_s^2 \pi / (P_s V_s^2 + 1))^2 \quad (3)$$

where subscript p represents the polymer and subscript s represents the solvent. P_s , T_s , and V_s are the reduced pressure, temperature, and the volume respectively. The difference in the free volumes of the mixture components is given by

$$\tau = 1 - T_s^*/T_p^* \quad (4)$$

The v^2 parameter is a measure of the difference in the chemical nature of the mixture components. In this study v^2 is fit to experimental data. The parameter π is defined as

$$\pi = P_s^*/P_p^* - 1 \quad (5)$$

The parameter $3c$ represents the number of external degrees of freedom of the solvent molecule. This parameter is calculated using

$$c = P^* V^* / RT^* \quad (6)$$

Finally the parameters U_s and $C_{p,s}$ are the reduced configurational internal energy and the reduced configurational heat capacity of the solvent, respectively. Using a van der Waals type of configurational internal energy,

$$U_s = -V_s^{-1} \quad (7)$$

the following expression is derived (16)

$$C_{p,s}^{-1} = (1 - 2/3 V_s^{-1/3}) - 2(1 - V_s^{-1/3}) / (P_s V_s^2 + 1) \quad (8)$$

and

$$T_s = (P_s V_s + V_s^{-1})(1 - V_s^{-1/3}) \quad (9)$$

The reduced temperature T_s is defined as

$$T_s = T/T_s^* \quad (10)$$

The critical mixture curve (i.e., LCST curve) is calculated in the following manner. First the reduction parameters are determined from pure component P-V-T data, (see ref. 15), then the parameters τ , π , and c are determined. The parameter ν^2 , which affects the location of the UCST and the LCST curves, is then fitted to the LCEP by solving equations 1 through 10 (5). A non-zero value of ν^2 is needed to predict both an LCST and a UCST curve (17). Once ν^2 is determined, the rest of the critical mixture curve is calculated. The mixing rules for $\langle U^* \rangle$ and $\langle T^* \rangle$ as described by Patterson and Delmas (15) are used for the multicomponent solvents investigated in this study. These mixing rules are

$$\langle U^* \rangle = \sum_i x_i U_i^* \quad (11)$$

where x_i = mole fraction

$$1/\langle T^* \rangle = \sum_i x_i / T_i^* \quad (12)$$

$$X_i = x_i U_i / \langle U^* \rangle \quad (13)$$

The mixing rule for $\langle P^* \rangle$ is

$$\langle P^* \rangle = \sum_i \sum_j X_i X_j P_{ij}^* \quad (14)$$

$$P_{ij}^* = (P_i^* P_j^*)^{1/2} \quad (15)$$

Based on our results the calculated phase diagram is not extremely sensitive to the form of the mixing rule for $\langle P^* \rangle$.

To test Patterson's model the critical mixture curves for the previously reported poly(ethylene-co-propylene) (EP) - hexane - ethylene system are determined (13). The EP - hexane - ethylene system is modelled since a large body of data are available. Although the EP polymer has a polydispersity of 2.2 and the hexane is actually an isomeric mixture of C_6 's, these mixtures exhibit phase behavior which is similar to that of the previously described polystyrene - toluene - SCF mixtures. For these calculations the pure component characteristic parameters for supercritical ethylene are fitted to a function of temperature and pressure using pure component data (i.e., the isothermal compressibility and the thermal expansion coefficient). The modelling results are shown in Figure 8. In general the calculated LCST curves are in agreement with the experimentally determined curves. Notice, however, for the case of 30.0 wt% ethylene it appears that the LCST and UCST curves are merged. If the LCST curve is extrapolated to lower temperatures, the intersection of the LCST curve with the extrapolated LLV curve occurs at approximately 150 K. The LCST curve probably merges with the UCST curve before reaching such cold temperatures. The model also predicts the merging of the UCST and the LCST curves although the shape of the curve is not quantitatively represented.

As shown in Figure 8 the fitted ν^2 values are small positive numbers except for the case without SCF additive. This negative ν^2 value is physically unrealistic and is probably a consequence of determining hexane's pure component characteristic parameters at a fixed temperature of 25°C. Also, in these calculations the polydispersity of the EP polymer is not incorporated

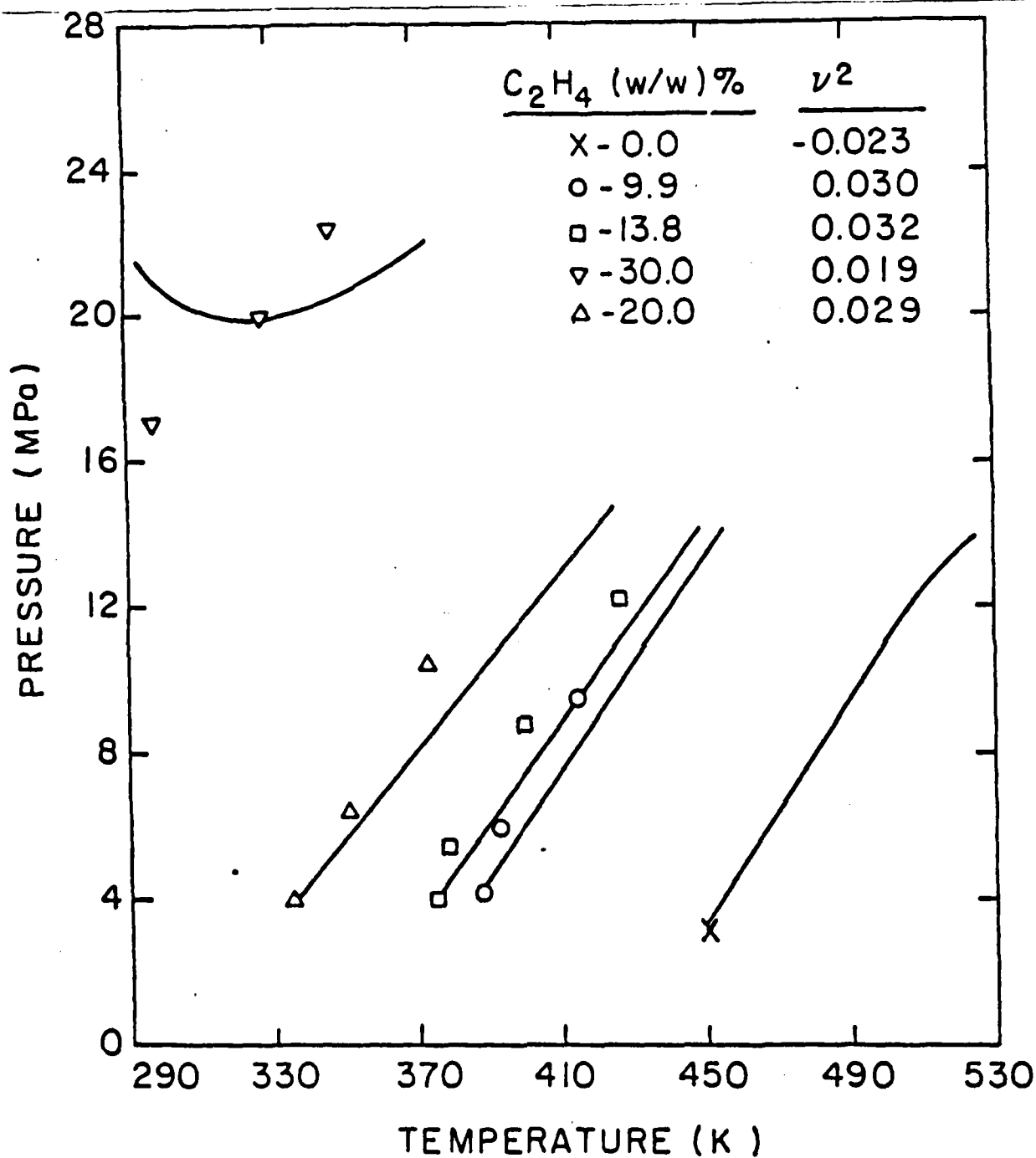


Figure 8. Comparison of the calculated and experimental LCST curves for the poly(ethylene-co-propylene)-hexane-ethylene system.

into the model. As shown by Koningsveld substantial errors in the calculations can result if the polydispersity of the polymer is not taken into account (18). It is encouraging then that the calculations that are performed for the EP - hexane - ethylene system are in reasonable agreement with the data.

Calculations for the polystyrene - toluene - SCF systems are in progress. This system should offer a less extreme test of the theory since the polystyrene used in this study is fairly 'monodisperse'.

CONCLUSIONS

Polymer solutions can be separated by an LCST phase split as an alternative method to steam stripping. Adding an SCF additive to the polymer solution shifts the LCST curve to lower temperatures, decreasing the thermal energy costs of the phase split and reducing the possibility of thermally degrading the polymer.

The phase behavior of polymer solutions is qualitatively interpreted in terms of the phase behavior of simple binary mixtures. However, with a binary system there is a three-phase line while for the polymer solutions there is a three-phase region. The three phase-region is a consequence of the multicomponent nature of the polymer solution.

The phase behavior presented in this paper are also interpreted using the corresponding states model of Patterson. Reasonable results are obtained, including the prediction of the merging of the LCST and UCST curves. Better predictions are expected when the polydispersity of the polymer is explicitly taken into account.

ACKNOWLEDGEMENT

Acknowledgement is made for the partial and technical support of the Exxon Chemical Company. This work is supported in part by the Office of Naval Research.

NOMENCLATURE

c	Prigogine parameter: a measure of the external degrees of freedom
C_p	Reduced heat capacity
L	Liquid phase region
LCEP	Lower critical end point
LCST	Lower critical solution temperature
LL	Two phase liquid-liquid region
LLV	Three phase liquid-liquid-vapor region
LV	Two phase liquid-vapor region
M_n	Number average molecular weight
M_w	Weight average molecular weight
P	Reduced pressure
r	Parameter defined by equation 2: a measure of the polymer-solvent size difference
R	Universal gas constant
SCF	Super critical fluid
T	Reduced temperature
U	Reduced configurational internal energy
UCEP	Upper critical end point
UCST	Upper critical solution temperature
V	Reduced volume
x	mole fraction
X	energy fraction
$\langle \rangle$	averaged property

greek symbols

π	parameter defined by equation 4: accounts for high hydrostatic pressures
τ	parameter defined by equation 3: accounts for free volume difference between solvent and polymer
χ	Flory parameter
ν	fitted parameter: a measure of the chemical difference between solvent and polymer

subscripts

i	component i
c	critical
p	polymer
s	solvent

superscripts

$*$	reduction parameter
-----	---------------------

REFERENCES

1. P. I. Freeman, and J. S. Rowlinson, *Polymer*, **1**, 20 (1960).
2. J. M. Bardin, and D. Patterson, *Polymer*, **10**, 9 (1967).
3. C. H. Baker, W. B. Brown, G. Gee, J. S. Rowlinson, D. Stubley, and R. E. Yeadon, *Polymer*, **3**, 215 (1962).
4. C. H. Baker, C. S. Clemson, and G. Allen, *Polymer*, **1**, 5255 (1966).
5. L. Zeman, and D. Patterson, *J. Phys. Chem.*, **76**, 1214 (1972).
6. G. Allen, and C. H. Baker, *Polymer*, **6**, 181 (1965).
7. S. Saeki, S. Konno, N. Kuwahara, M. Nakata, and M. Kaneko, *Macromolecules*, **7**(4), 521 (1974).
8. J. M. G. Cowie, and I. J. McEwen, *Macromolecules*, **7**(3), 291 (1974).
9. C. D. Myrat, and J. S. Rowlinson, *Polymer*, **6**, 645 (1965).
10. P. Ehrlich, and J. J. Kurpen, *J. Polym. Sci., part A*, **1**, 3217 (1963.)
11. C. A. Irani, C. Cozewith, and S. S. Kasegrande, U.S. Patent 4,319,021 (1982).
12. L. Zeman, J. Biro, and D. Patterson, *J. Phys. Chem.*, **76**, 1206 (1972).
13. M. A. McHugh, and T. L. Guckes, *Macromolecules*, in press (1985).
14. S. Saeki, S. Konno, N. Kuwahara, M. Nakata, and M. Kaneko, *Macromolecules*, **7**(4), 521 (1974).
15. D. Patterson, and G. Delmas, *Trans. Faraday Soc.*, **65**, 708 (1969).
16. P. J. Flory, *Disc. Faraday Soc.*, **49**, 7 (1970).
17. K. S. Slow, G. Delmas, and D. Patterson, *Macromolecules*, **5**, 29 (1972).
18. R. Koningsveld, and A. J. Staverman, *J. Polymer Sci., A-2*, **6**, 305 (1968).

END

FILMED

7-85

DTIC