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Phase Equilibria of Polymer–Solvent Systems at High Pressures Near Their Critical Loci: Polyethylene with *n*-Alkanes*

PAUL EHRLICH† and JOHN J. KURPEN, *Monsanto Chemical Company, Plastics Division, Research Department, Springfield, Massachusetts*

Synopsis

Above the crystallization temperature slightly branched polyethylene and propane are miscible in all proportions above a critical pressure, defined as upper critical solution pressure (UCSP). This pressure decreases only very slightly from 110 to 150°C. At 110°C. the UCSP varies from 450 atm. for a polymer fraction of molecular weight 17,000, to 580 atm. for one of molecular weight 250,000. The critical polymer concentrations are low as in conventional polymer–solvent systems and shift with molecular weight in a similar manner. The pressures required to achieve solubility of the polymer in the gas at polymer concentrations less than critical (dew-point pressures) are nearly as high as the UCSP down to very low polymer concentrations. The data determine part of the critical locus in (P, T, composition) space. Experiments with other polyethylene–*n*-alkane systems (ethane, butane, and pentane) show that the critical locus changes gradually from a liquid–liquid to a gas–liquid boundary and might be termed a fluid-liquid locus. If crystallization of polymer does not intervene, this locus intersects the saturated vapor pressure curve at a lower critical end point (LCEP) which is the lower critical solution temperature (LCST) found only recently by Freeman and Rowlinson in many hydrocarbon polymers with hydrocarbon solvents. Incomplete miscibility extends over greater regions of temperature and pressure as the solvent molecule becomes smaller, but the critical locus would probably be closed along the pressure axis for a hypothetical amorphous polymethylene with ethane.

INTRODUCTION

We reported recently[1] that the phase equilibria of liquid high pressure polyethylene with compressed gases showed at least one of the usual characteristics of conventional polymer–solvent systems: a critical condition occurred at very low polymer concentration. This was associated with a change from negligible solubility of the polymer in the solvent to complete mutual miscibility over a small change in pressure. Polymers can therefore be completely miscible with compressed gases above a definite pressure[1,2] and the binary systems possess a gas–liquid critical locus in (P, T, composition) space.

Freeman and Rowlinson[3] found that hydrocarbon polymers heated

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† Central Research Dept., 800 N. Lindbergh, St. Lo

drocarbon solvents under their own vapor pressure show liquid-
mmiscibility above a lower critical solution temperature (LCST)
an be well below the critical point of the solvent. Such a LCST
he intersection of the vapor pressure surface with the critical locus
been termed a lower critical end point (LCEP). A LCST generally
es with pressure near this point, i.e., the critical locus has a positive
The solution of polymers in gases at high pressures is a possible
uence.

work to be reported explores this connection further and provides
n the conditions of solubility of polyethylene in *n*-alkane solvents
and below their critical temperatures. The data will be seen to
sh the general trends in the critical loci of binary alkane systems as
mponents assume extreme size differences.[5]

EXPERIMENTAL

Equipment

ure 1 describes the experimental arrangement. The optical bomb
supported inside a brass ring linked by a worm gear to a synchronous
notor. It could be rocked automatically around the horizontal posi-
n a plane perpendicular to the axis through either set of windows,
ould be positioned at any desired angle. The bomb was connected
arm of $^{1}/_{4} \times {}^{1}/_{16}$ in. tubing (B) and a coil (D) made of $^{1}/_{8} \times 0.020$ in.
g, with its plane parallel to the plane of rotation of the bomb, to the

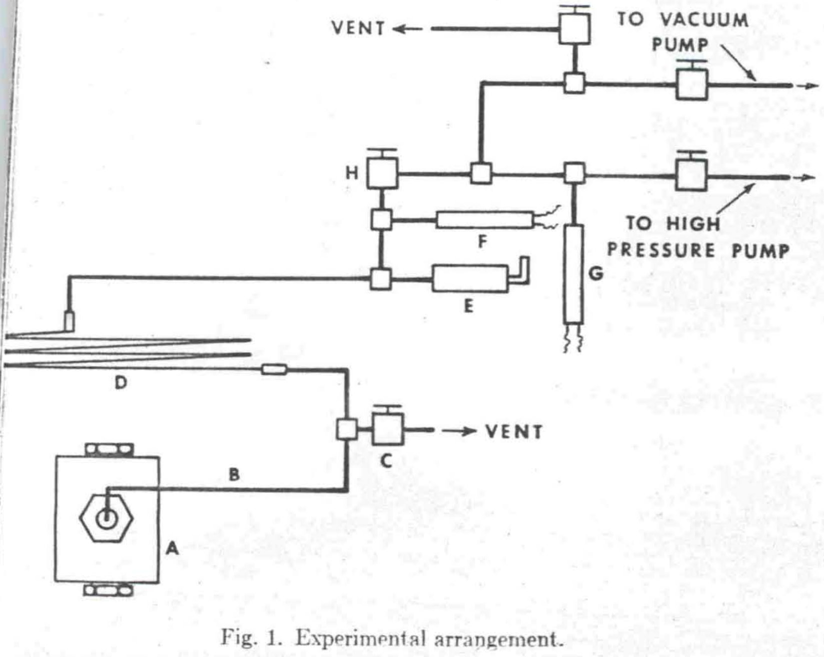


Fig. 1. Experimental arrangement.

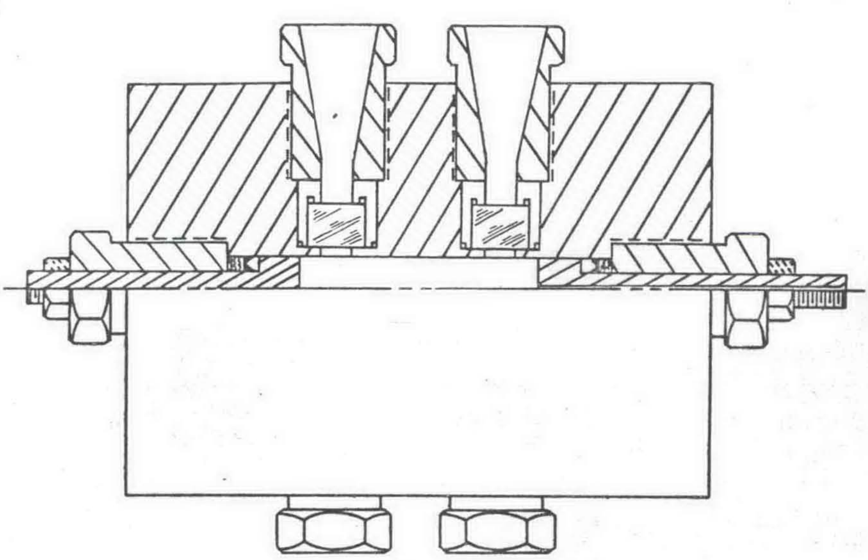


Fig. 2. Optical bomb.

filling system with connections to pressure transducers (F) and (G), vacuum line, and high pressure pump. (C) is a valve for venting.

The optical bomb (Fig. 2) was designed and built by the McCartney Mfg. Company (Baxter Springs, Kan.). It was made from 4340 double vacuum melt-forged steel and had two pairs of windows at 180° for viewing of the chamber by transmitted light. Windows (1 in. dia. × $^3/_4$ in.) made from Pyrex, Feurex, or plate glass were sealed by two sets of Neoprene O-rings, and the two end closures were of the Bridgman type. The main dimensions of the bomb cavity were 4 × 1 in., and the volume was 62 cc.

Pressure transducer (F) was of the SR-4 type (Baldwin, Lima, Hamilton) and read on a Dynalog (Foxboro Co.) Recorder. It measured the pressure in the optical bomb. Transducer G (Microsen Type 145: Manning, Maxwell and Moore) measured the pressure on the pump side of the system and transmitted it to an indicating voltmeter. E is a rupture disk assembly (American Instrument Company). The high pressure pump was an air operated piston pump (Type 4444-J: McFarland Mfg. Corp.). A Bourdon gauge (not shown) measured the pressure in the experiments with pentane.

The bomb (but not the coil D) could be brought to the desired temperature by immersion in an oil bath raised by an air piston. The bath temperature was sensed by a thermocouple and recorded. A steady pressure in the bomb indicated thermal equilibrium.

Materials

Six polyethylene fractions were obtained by solvent–non-solvent fractionation from a high pressure polyethylene with 1.7% methyl content, nd the data to be reported were obtained with the four center fractions. he heterogeneity of the fractions was not determined. Molecular eights were measured osmometrically for the two high fractions and obined from intrinsic viscosities[6] for the two low fractions. Ethane, *n*-ropane, and *n*-butane were obtained from the Matheson Company, hane at 99%, and *n*-propane and *n*-butane at 99.5% purity. *n*-Pentane as obtained from the Phillips Petroleum Company at 98.5% purity.

Procedure

A known weight of polymer and a steel ball, $^5/_8$ in. in diameter, were laced in the bomb which was then evacuated. Solvent was then compressed into the bomb (the pump chamber had to be cooled when ethane vas used) such that, upon bringing it to the desired temperature, the system vas at a pressure slightly greater than the anticipated dew-point or bubble-point pressure. When the desired temperature had been approached, he bomb was rocked. After the system had reached equilibrium in the one-phase region, it was vented slowly through valve C. Upon approaching the phase boundary, the transmitted light intensity diminished sharply, and a phase boundary became visible. The pressure interval over which hese phenomena took place varied from barely resolvable (2 atm.) to as much as 30 atm. with the lowest molecular weight fraction at low polymer concentrations. Where the interval was relatively broad, the pressure at which the sharpest intensity change took place was taken as the dew-point or bubble-point pressure. Prior to phase separation the solution sometimes showed a dark orange color by transmitted light, indicating the occurrence of critical scattering. This generally happened at concentrations where the solution, upon lowering the pressure, separated such that the lower phase occupied 30–50% of the volume. The phase volume at a pressure as close as possible to that at which the phases separated was determined by means of a prior calibration of bomb angle versus phase volumes. During a run valve H was closed and, strictly speaking, the experimental system extended to that point. However, there was very little diffusion of polymer out of the bomb, and none into the coil. The volume between the bomb and the valve C was only about 1 cc., and the concentration change due to venting was always small. Concentration changes due to diffusion and venting were therefore ignored in the calculation.

The amount of solvent charged into the bomb was not measured. It was calculated for propane from the data of Reamer, Sage, and Lacey,[7] assuming no volume change of mixing. Since a negative volume change of mixing is, in fact, likely, this introduces an error into the calculation of weight per cent polymer. The isotherms, however, are reported at low polymer concentrations only, and judging from other experiments carried out in this laboratory, the error is not believed to exceed 10% at the highest polymer concentrations reported, and should be considerably less at the critical concentration. The critical conditions are also reported as volume fraction polymer, defined here as volume of pure polymer at the temperature and pressure of the experiment[8] divided by the volume of the vessel. This description lacks physical reality in systems with volume changes of mixing, but will be made use of, since the critical conditions in lattice theories are described in terms of volume fractions. With solvents other than propane where only the critical loci, and not the isotherms, were determined, there was no need for accurate determinations of the weight or volume fractions.

RESULTS

Phase Behavior of Polyethylene–*n*-Propane

Perhaps the most characteristic feature of the system polyethylene–*n*-propane at 110°C. is the existence of a pressure, above which a single phase exists, and which is an only slowly varying function of composition at low polymer concentrations. This pressure is a dew-point or bubble-point pressure and may be represented by means of an isotherm, i.e., by a (pressure–composition) section of the three-dimensional model (Fig. 3).

The maximum pressure on the isotherm which also corresponds to incipient separation of two phases of equal composition is an upper critical solution pressure (UCSP). Since the curve is nearly flat near the UCSP, this pressure is easily determined, whereas the corresponding critical poly-

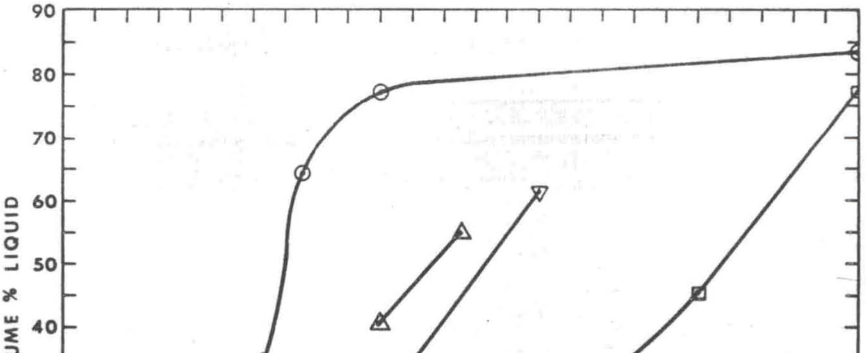


Fig. 3. Phase volumes at phase separation as a function of polymer charge for polyethylene-*n*-propane at 110°C.: (⊙) fraction 2; (△) fraction 3; (▽) fraction 4; (□) fraction 5.

concentration is not. The experimental error in the dew-point and ble-point pressures is such that the maximum cannot be located along composition axis by inspection. Instead, the weight fraction W_c' olume fraction ϕ'_c of polymer at which the system breaks up into two ses of equal volumes can be located approximately from a plot of phase ume just below the isotherm as a function of composition (Fig. 3). convenience, this is termed the apparent critical composition. The critical concentration cannot be very far from the apparent critical centration for two reasons: relative phase volumes change rapidly h composition (Fig. 3) and only extreme dissymmetry in the pressure-position diagram close to the critical point could lead to a wide diverce between the two points. Also, although no attempt was made to ne exactly the concentration range in which critical scattering occurred, solutions which were darkest in color by transmitted light generally urred at concentrations such that the lower phase occupied 30–50% of volume. It seems legitimate to conclude that whereas W_c might sibly be as much as 30% lower than W'_c, it cannot greatly exceed the ues of W'_c listed because of the noticeable drop in pressure on the iso-rm (pressure–composition section) at concentrations greater than W'_c.

able I presents the critical pressures and apparent critical compositions four fractions of molecular weight 17,000–250,000 at 110°C. The ical points are seen to occur at low polymer concentrations, a situation ical for polymer–solvent systems. The critical pressures converge for high fractions, suggesting the existence of a limiting value for polymer infinite molecular weight. According to the Flory-Huggins theory,[9] critical concentrations are given approximately by $x^{-1/2}$, where x is ratio of molecular volumes of polymer and solvent. The apparent ical concentrations are seen to exceed $x^{-1/2}$, but the dependence is ap-ximately of the form required.

he existence of a second, and higher, critical pressure at which the system in breaks up into two phases is conceivable. This, according to ndard terminology, would be a lower critical solution pressure. No h phenomenon was encountered with the highest molecular weight tion at pressures up to 2,000 atm. at 130–150°C.

TABLE I

er Critical Solution Pressures and Critical Polymer Concentrations for Fractions of Polyethylene in Propane at 110°C.

signation of fraction	Molecular weight of fraction	Critical pressure, atm.	Apparent critical concentration of polymer		$x^{-1/2}$
			Wt. fraction	Vol. fraction	
2	246,000	582	0.042	0.027	0.017
3	89,000	561	0.072	0.045	0.028
4	37,000	531	0.082	0.054	0.044
5	17,000	449	0.129	0.090	0.066

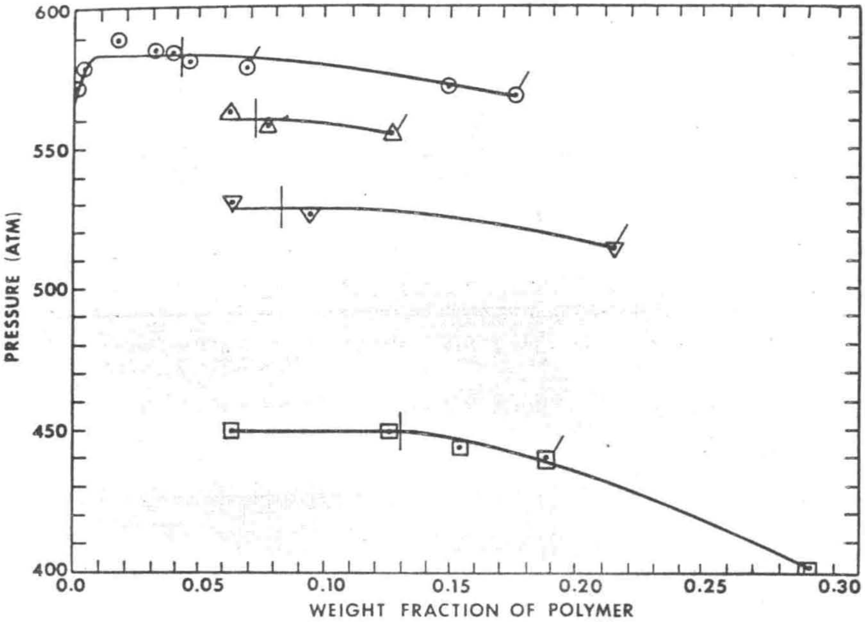


Fig. 4. Pressure-composition section for polyethylene-*n*-propane at 110°C.: (⊙) fraction 2; (◬) fraction 3; (⛛) fraction 4; (⊡) fraction 5. Bubble-point and dew-point pressures by direct observation (unprimed symbols); by calculation from phase volumes in two-phase region primed symbols. Vertical lines indicate apparent critical composition.

The effect of temperature on the UCSP is small. Several of the fractions were investigated up to 150°C., and although UCSP's at that temperature appeared to be lower, the effect was only slightly greater than the experimental error. In none of the systems studied was the UCSP lowered by more than 15 atm. in going from 110 to 150°C. In going to the higher temperature, the critical point appeared to shift only very slightly toward higher polymer concentrations.

At polymer concentrations less than critical the pressure on the phase boundary (dew-point pressure) was found to be very close to the critical pressure down to extremely low polymer concentrations. Thus, for fraction 2, dew-point pressures within experimental error of the UCSP were found for polymer concentrations down to 0.3, and possibly 0.15 wt.-% (0.2 and 0.1 vol.-%). On the low concentration side, the phase boundary runs along the pressure axis up to pressures closely approaching the UCSP. This makes it possible to estimate the phase diagram at pressures below the UCSP by determining the location of the meniscus and by assuming the critical composition to occur with the meniscus at 50 vol.-% bomb contents. The pressure–composition diagrams are shown in Figure 4. Points obtained by the less reliable method just described fall on the same plots as those obtained by the direct measurement of dew-point and bubble-point pressures.

stigated in detail, should be given by the change in melting point of
ethylene with pressure[8] and with dilution.[10]

ith pentane (Fig. 6), the critical locus can be followed down to the
er critical end point (LCEP), or the lower critical solution temperature
ST) on the vapor pressure curve, where two liquid phases and a gas
se coexist.[3] This point lies at 91 °C. at a pressure indistinguishable from
vapor pressure of the pure solvent by the present method of measure-
nt. Freeman and Rowlinson[3] did not attain complete miscibility in
system polyethylene–*n*-pentane, probably because they operated with
ar polyethylene where the crystallization boundary was shifted to
her temperatures, intersecting the critical locus above the LCEP.

t is clear that a LCEP of high molecular weight polyethylene exists only
n-alkanes with five carbons and greater because of an increase in the
EP with size of the solvent molecule and because of the increase in
lting point of the polymer with pressure.

DISCUSSION

All systems reported are characterized by a large free volume and by
ge density differences between the components. There also should be a
gative volume change of mixing ΔV along a critical locus of the type
scribed. Every point on this locus, denoted by subscript c, may be con-
dered as LCST with $(dP/dT)_c > 0$ or as UCST with $(dP/dT)_c < 0$.
ertain inequalities involving the second derivatives with respect to
mposition of the thermodynamic mixing functions must be satisfied
ong the locus and, if there are no points of inflection, one has at an LCST
$H < 0$, $\Delta S < 0$ and at an UCST $\Delta H > 0$, $\Delta S > 0$.[4] These latter con-
itions have been verified near an LCST in several cases.[11,12] In addition,
$P/dT)_c$ is given by

$$\frac{\partial^2 \Delta S}{\partial x_2^2} \Big/ \frac{\partial^2 \Delta V}{\partial x_2^2}$$

here x_2 refers to the mole fraction of solute.

Clearly, all lattice treatments of polymer solutions seem here less satis-
ying physically than under ordinary conditions and violate one or more of
he inequalities which must be met along the critical locus, particularly
here $(dP/dT)_c > 0$. One objection to the use of the results obtained
rom lattice treatments is removed, when it is realized that expressions
or the free energy of mixing formally identical to that of the Flory-Huggins equation have been obtained by considerations not requiring the lattice assumption.[13,14] In order to allow for negative, as well as positive, heats of mixing the Flory-Huggins interaction parameter χ must be considered as a free energy,[11] as indeed required by the more general lattice treatments[15] and by the theory of Longuet-Huggins.[13] Patterson[11] has suggested further that χ, although no longer a heat term, may still be identified with Hildebrand's solubility parameter term, which then becomes

a free energy, too. It seems therefore not unreasonable to discuss critical mixing in terms of the critcal conditions derived from the Flory-Huggins theory ($\chi_c = 0.5$ for polymer of infinite molecular weight), and to expect χ_c to be given approximately by the solubility parameter term.

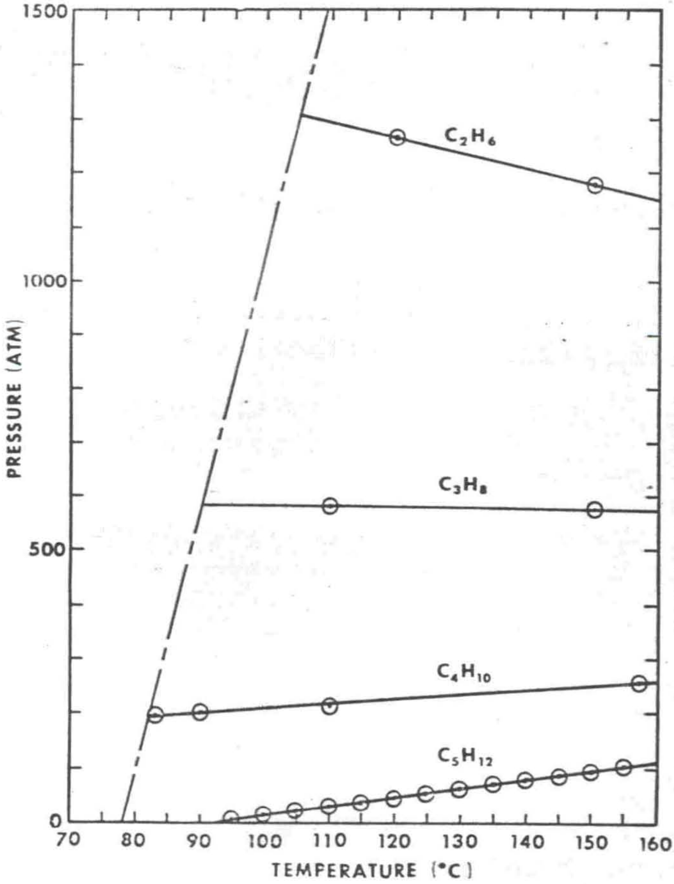
Assuming the volume of change of mixing not to be excessive, the solubility parameter for a gas can be calculated by substituting its energy of compression, ΔE_1, for the energy of vaporization[1] of the standard treatment. The solubility parameter for the solvent, δ_1, is then taken to be the square root of the cohesive energy density, $\Delta E_1/V_1$, where V_1 is the molar volume of the solvent. Table II lists the solubility parameters at the UCSP, calculated by means of a reduced variable correlation.[16] δ_1 is seen to vary with temperature, but to be nearly constant at a given temperature for all alkanes studied, although a slight drop with the size of the solvent molecule seems indicated. If one uses the value of Allen et al.[17] for an amorphous linear polyethylene (δ_2 is 8.37 cal.$^{1/2}$ cc.$^{-1/2}$ at a density of 0.855 g. cc.$^{-1}$), and allows δ_2 to vary as $a^{1/2}/V_2^{-1}$ (van der Waals fluid behavior), one obtains values of χ in the range of 0.4–0.8. Positive deviations from 0.5 increase with the size of the solvent molecule and with temperature. The data are, therefore, not quantitatively consistent with the approach outlined. A very rough estimate of the UCSP from the thermodynamic properties of the components is, however, possible. In the n-alkane–polyethylene systems investigated, furthermore, the UCSP for a given solvent at a given temperature is evidently calculable with reasonable accuracy from that of another by assuming critical mixing to occur at a fixed value of δ_1. Note, however, that at least equally successful a calculation could be made in terms of reduced densities (Table II).

The critical locus of binary alkane systems whose components differ only moderately in size is a continuous unbroken line joining the critical points of the pure components. Katz and Rzasa[5] in a detailed optical study of methane with an oil fraction containing mostly C_{20} paraffin, have shown that, as the size difference between the components increases, the maximum pressure on the critical locus rises and is shifted toward the component of low molecular weight. Freeman and Rowlinson,[3] however, found that solutions of hydrocarbon polymers in hydrocarbon solvents, upon heating under their own vapor pressures, break up into two liquid phases at a LCST which can be well below the critical point of the solvent. This LCST must also be the lower critical end point (LCEP) of the critical locus which, if closed along the pressure axis, must change gradually from a liquid–liquid to a gas–liquid boundary.[4] This lack of sharp distinction between liquid and gaseous solvents is demonstrated in this study which shows sections of the critical locus of polyethylene with solvents which are above, below, and close to their critical temperatures. The slope of the critical locus at a given temperature differs in sign and magnitude (Table II, Fig. 5); it is close to zero, but slightly negative, with propane just above its own critical point of 97°C. This suggests that the critical

Critical Loci of Polyethylene–n-Alkane Systems

The bubble- or dew-point pressures were also determined for the highest olecular weight fraction with ethane, butane, and pentane at several mperatures (Table II). These runs were carried out at about 5 wt.-% lymer, although not exactly at the critical polymer concentration. ecause of the flatness of the dew-point–bubble-point curve near the UCSP d because of the slow shift in critical concentration with temperature, e pressures on the phase boundary are within experimental error of the CSP and are listed as such. It is now clear that the data of Table I and able II define sections of the critical locus for all systems investigated. hese critical loci, i.e., the P, T projections of the (P, T, composition) space odels, are shown in Figure 5.

With all solvents except pentane, solid precipitates at about 90–110°C., here the vapor pressure curve of the partly amorphous and partly crystal-ne polymer intersects the critical locus. The point of intersection, not



ig. 5. Critical loci for polyethylene–n-alkane systems. The broken line indicates approximate crystallization boundary.

TABLE II

Some Thermodynamic Parameters of Some *n*-Alkanes at the UCSP with a Polyethylene Fraction of Molecular Weight 246,000

n-Alkane	Critical temperature of solvent, °C.	Reduced density	UCSP, atm.	T, °C.	Solubility parameter δ_1, (cal./cc.)$^{1/2}$
Ethane	32	2.32	1,270	120	6.18
		2.15	1,180	150	5.73
Propane	97	2.275	582	110	6.30
		2.15	575	150	5.72
Butane	152	2.32	204	110	6.12
		2.15	255	157	5.60
Pentane	197	2.35	34.3	110	5.91
		2.25	50	120	5.73
		2.175	89.5	150	5.51

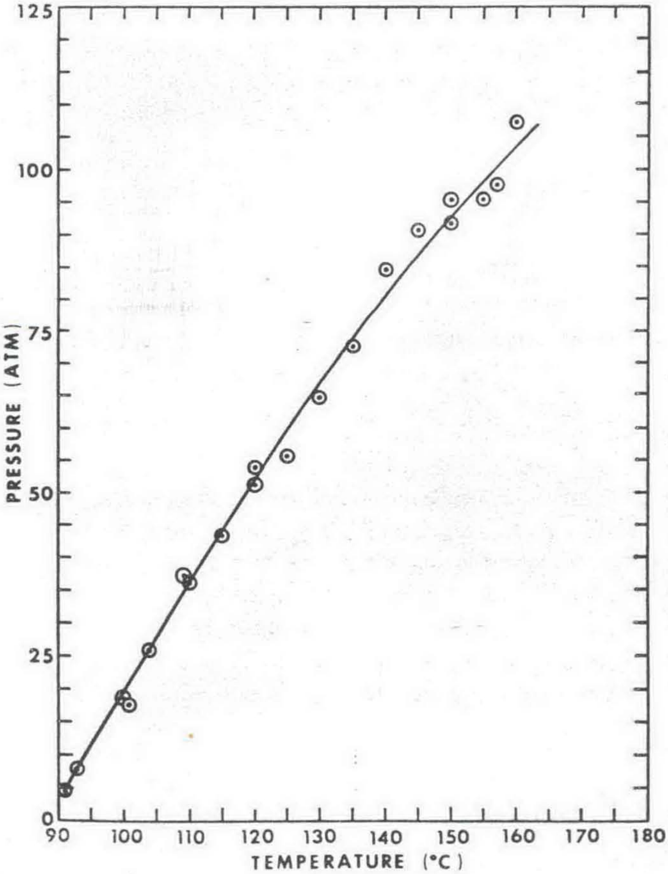


Fig. 6. Critical locus for polyethylene–*n*-pentane.

us has its maximum pressure near the critical temperature of the solvent l, barring crystallization of polymer, is closed at the top (along the pres- e axis). The size of the dome of immiscibility evidently increases as size of the solvent molecule is reduced. The pressure maximum for ane with a hypothetical amorphous polymethylene of infinite molecular ight would be presumably in the neighborhood of 1500 atm. Whereas points on the critical locus may be referred to as lower and upper critical ution temperatures, the term upper critical solution pressure is perhaps re descriptive, since the critical locus extends over a great temperature ge at a pressure which varies only slowly. This locus is best described a fluid–liquid locus. It must be distinguished, of course, from the very rt gas–liquid locus which extends presumably over a range of several grees centigrade at most between the critical point of the pure solvent and e upper critical end point (UCEP).[3] Every point on the fluid–liquid us for polymer of infinite molecular weight satisfies Flory's definition of a point.

Physically, the critical phenomena and shapes of the critical loci described re may be attributed to the high coefficients of thermal expansion and thermal compressibility of the solvents near or above their critical ints. In the more familiar case where an UCST is not the result of ese conditions, such as with polystyrene–cyclohexane near room tempera- re, the slope of the critical locus, $(dP/dT)_c$, can be by one or two orders of agnitude greater and opposite in sign.[18]

We are indebted for discussions to Dr. D. C. Chappelear and to Professor J. S. Rowlin- n who also pointed out the relevance of his work on the LCST to the solubility of lymers in gases. We are also grateful to Messrs. R. A. Isaksen and C. Crofoot for pre- ring the polyethylene fractions.

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Résumé

Au-dessus de la température de cristallisation le polyéthylène légèrement ramifié et le propane sont miscibles en toutes proportions au-dessus d'une pression critique définie comme la pression critique supérieure de solution (UCSP). Cette pression décroît seulement très faiblement de 110° à 150°C. A 110°C l'UCSP varie de 450 atmosphères pour une fraction de polymère de poids molèculaire 17.000 à 580 atm. pour une fraction de poids moléculaire 250.000. Les concentrations critiques en polymères sont basses comme dans des systèmes conventionnels polymère–solvant et changent de même façon avec le poids moléculaire. Les pressions requises pour solubiliser le polymère dans le gaz à des concentrations critiques (pressions du point de rosée) sont presqu'aussi élevées que le UCSP jusqu'à des concentrations très basses en polymère. Les résultats déterminent une partie du lieu critique dans l'espace (composition *P*, *T*). D'autres expériences avec d'autres systèmes polyéthylène–*n*-alcane (éthane, butane et pentane) montrent que le lieu critique change graduellement d'une séparation liquide–liquide vers une séparation gaz–liquide et peut être appelé un lieu fluide–liquide. S'il n'intervient pas de cristallisation du polymère, ce lieu intersepte la courbe de la tension de vapeur saturée à un point critique terminal inférieur (LCEP) qui est la température critique inférieure de solution (LCST) trouvée tout récemment par Freeman et Rowlinson dans beaucoup de polymères hydrocarbonés avec des solvants hydrocarbonés. La miscibilité incomplète s'etend sur des plus grandes régions de température et de pression lorsque la molécule de solvant devient plus petite, mais le lieu critique serait probablement fermé au long de l'axe des pressions pour un unpolyméthylène amorphe hypothétique avec l'éthane.

Zusammenfassung

Oberhalb der Kristallisationstemperatur sind schwach verzweigtes Polyäthylen und Propan oberhalb eines kritischen, als oberer, kritischer Lösungsdruck (UCSP) definierten Druckes in allen Verhältnissen mischbar. Dieser Druck nimmt im Bereich von 110° bis 150°C nur sehr wenig ab. Bei 110°C steigt der UCSP von 450 Atmosphären für eine Polymerfraktion vom Molekulargewicht 17000 auf 580 Atmosphären für eine solche vom Molekulargewicht 250000 an. Die kritische Polymerkonzentration ist, ähnlich wie in konventionellen Polymer–Lösungsmittelsystemen, niedrig und vom Molekulargewicht abhängig. Die für eine Löslichkeit des Polymeren in der Gasphase bei Polymerkonzentrationen kleiner als der kritischen erforderlichen Drucke (Taupunktsdrucke) sind bis zu sehr kleinen Polymerkonzentrationen fast so hoch wie die UCSP. Die Daten bestimmen einen Teil des kritischen Ortes im (*P*, *T*, Zusammensetzungs)-Raum. Versuche mit anderen Polyäthylen–*n*-Alkansystemen (Äthan, Butan, Pentan) zeigen, dass das kritische Gebiet allmählich von einer Flüssig–Flüssig- zu einer Gas–Flüssiggrenze übergeht und als Fluid-flüssig–Ort bezeichnet werden kann. Falls keine Kristallisation des Polymeren auftritt, schneidet dieses Gebiet die Sättigungsdruckkurve bei einem unteren kritischen Endpunkt (LCEP), welcher mit der erst vor kurzem von Freeman und Rowlinson bei vielen Kohlenwasserstoffpolymeren mit Kohlenwasserstofflösungsmitteln gefundenen unteren kritischen Lösungstemperatur (LCST) identisch ist. Mit abnehmender Grösse der Lösungsmittelmoleküle erstreckt sich die begrenzte Mischbarkeit über grössere Temperatur- und Druckbereiche; bei einem hypothetischen amorphen Polyäthylen würde aber wahrscheinlich mit Athan der kritische Ort der Druckachse entlang geschlossen sein.

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