Phase Equilibria of Linear Polyethylene with Supercritical Propane

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ABSTRACT: Cloud-point data and solid–supercritical fluid equilibria are reported for two fractions of linear and for unfractionated nearly linear polyethylene with supercritical propane at temperatures from about 110 to 130 °C and to pressures of about 650 bar. The data cover the temperature range just below and just above that of the second critical end point that lies at the intersection of the solid–liquid–vapor equilibrium lines that originate at the polymer's triple point with the vapor–liquid critical locus. For a fairly high molecular weight fraction ($\bar{M}_n$ = 100 500, $\bar{M}_w$ = 119 600), that point is estimated to lie at 118 °C and 640 bar.

I. Introduction

At a sufficiently high pressure and at temperatures greater than those that allow the polymer to crystallize, polyethylene is known to be completely miscible with ethylene, ethane, and the higher paraffins, even though these solvents may be above their critical temperature.[1] The polymer may then be said to be completely soluble in the compressed solvent gas beyond a cloud-point pressure which, in the case of a perfect fraction, is analogous to an upper critical solution temperature or Flory θ temperature. For an unfractionated polymer, the critical pressure, where a liquid and a vapor phase of equal composition coexist, does not coincide with the maximum on the cloud-point pressure vs composition isotherm but lies at polymer compositions higher than critical, again in analogy with the cloud-point temperature vs composition isobar typical of polymer solutions in liquid solvents, normally referred to as cloud-point curves. At pressures less than the cloud-point pressure, vapor–liquid (V–L) equilibrium exists. At lower temperatures the polymer crystallizes, and one then enters a region where crystalline polymer coexists with an extremely dilute solution of polymer in the supercritical solvent (S–SCF equilibrium) in the absence of a liquid phase. The data to be reported can be visualized in terms of a generic phase diagram for a perfect polymer fraction, somewhat in the spirit of the Bakhuis–Roozeboom diagrams of Koningsveld and Diepen[2] (Figure 1), together with the projections of critical and three-phase (S–L–V) lines (Figure 2) for the case where the three-phase equilibrium displays a minimum in temperature. The case of a low molecular weight organic solute is also shown in Figure 2 for comparison.

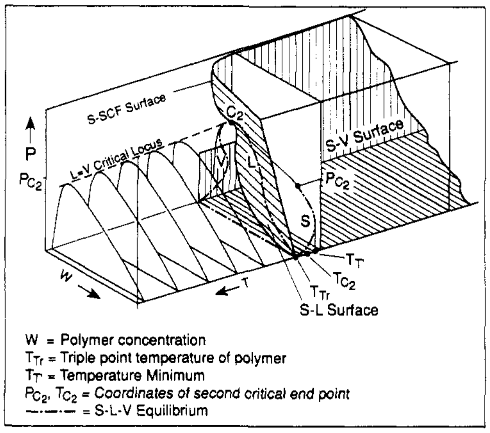

Figure 1. Generic phase model for a perfect fraction of a crystalline polymer and a solvent with which it is completely miscible in the supercritical phase. The model is applicable to polyethylene–propane.

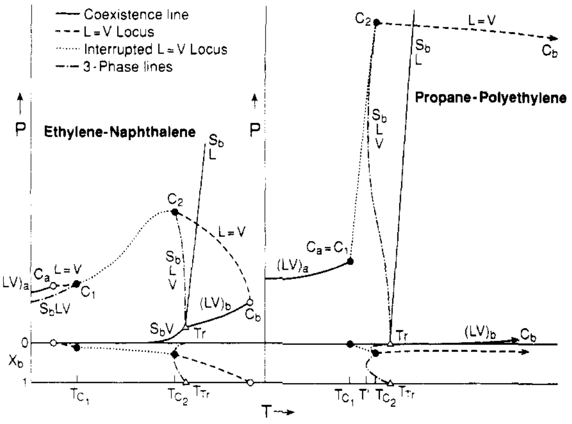

Figure 2. Projections of critical and three-phase lines for the model shown in Figure 1, in comparison with that for a low molecular weight solute.

Polymer fractionation with respect to molecular weight by partition between a supercritical fluid and a liquid phase has been accomplished in numerous cases,[3] and it was felt that fractionations, with respect to structure, e.g., branch content, might be performed in the region of S–SCF equilibrium. It was therefore of interest to study both fluid-fluid (cloud-points) and S–SCF equilibria of crystalline polyethylene. As solvent we chose propane because it represented the largest paraffinic solvent (and hence required the lowest pressure for complete polymer solubilization) whose critical temperature was less than the temperature at which polyethylene was expected to crystallize. This condition permitted us to meet the phase situation normally favored in supercritical extraction processes, i.e., the coexistence of solid and supercritical fluid in the absence of a liquid phase, at any pressure. [Fractionations under conditions of S–SCF equilibrium are nonetheless feasible under conditions where V–L phase separation would take place at a lower pressure.] We measured S–SCF equilibria and cloud points of propane with several fractions, as well as with unfractionated high

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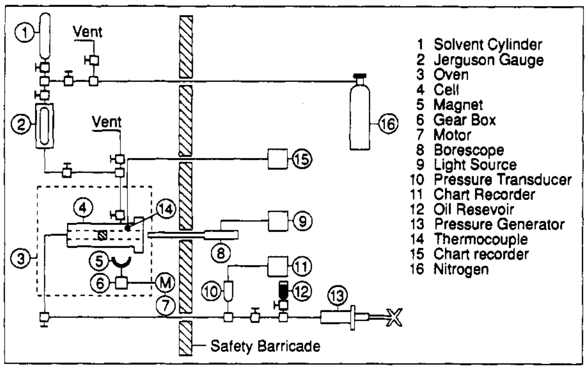

Figure 3. Experimental arrangement.

density (unbranched) polyethylene which allowed us to amplify the data base for phase equilibria of polymers with compressed fluid solvents where infinite or large solubility exists. The most exhaustive study of this type published so far is that for polyethylene–ethylene by de Loos et al.[4,5]

The data to be reported should be useful for the design of fractionation processes and for controlling polymer crystallization from supercritical solution, which can be accompanied by gelation.[6] The experimental method chosen was that of measuring P–T isopleths (coexistence curves) in both the S–SCF and L–V regions. Isopleths from the latter region were then replotted as isotherms of cloud-point pressures vs composition ("cloud-point curves").

II. Experimental Section

1. **Materials.** The polymer samples used were a low and a high molecular weight fraction of the National Bureau of Standards (NBS), now NIST, Reference Materials of linear polyethylene, designated linear polyethylenes 1482, 1483, and 1484, and a commercial, unfractionated high density (nearly linear) polyethylene HDPE 1. [Exact characterization of nearly linear polyethylene is difficult, both structurally (branch content) and thermodynamically (melting points). Nonlinear structures in our samples could lower S–SCF phase lines by several °C, but should have no measurable effect on cloud-point pressures compared to those of high molecular weight perfectly linear structures.] Fraction 1482 was reported to have $\bar{M}_n$ = 11 400 and $\bar{M}_w$ = 13 600; fraction 1483 $\bar{M}_n$ = 28 900 and $\bar{M}_w$ = 32 100, and fraction 1484 $\bar{M}_n$ = 100 500 and $\bar{M}_w$ = 119 600.[7] The molecular weight distribution of HDPE 1 was measured in this laboratory by gel permation chromatography (GPC),[8] yielding $\bar{M}_n$ = 7300, $\bar{M}_w$ = 42 900, $\bar{M}_z$ = 139 000, as were those of the fractions, yielding satisfactory agreement with the molecular weight averages reported by NBS. The detailed distribution curves of all samples, measured by GPC, are available.[8] The estimated branching content of HDPE 1 is 0.5 short-chain branches/100 C atoms. Instrument-grade propane was obtained from the Linde Division of Union Carbide Co. and had a stated purity of 99.5% or better.

2. **Method and Apparatus.** The method of isopleths pioneered by Diepen et al. in their exhaustive studies of naphthalene with ethylene[9] requires the determination of families of pressure (*P*) vs temperature (*T*) lines, one set for each solvent–solute composition, at which the transition from a single-phase to a two-phase system occurs. Such measurements require a variable-volume cell and the visual observation of the appearance or the disappearance of a liquid–vapor meniscus (cloud points) or the appearance or disappearance of solid. Since polymers cannot crystallize without considerable supercooling, the disappearance of the solid polymer upon slow heating had to be chosen to determine the S–SCF coexistence lines. Both types of equilibria could be measured in the variable-volume view cell[10] and associated apparatus depicted in Figure 3.

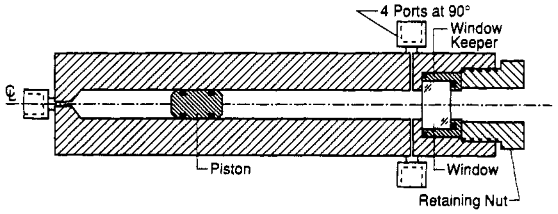

Figure 4. Variable-volume view cell.

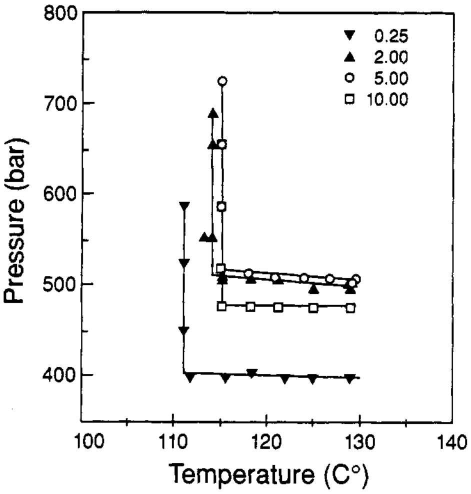

Figure 5. Cloud-point isopleths for fraction 1482. Concentrations specified near right top of Figures 5, 6, and 7 are expressed in wt % of polymer.

The view cell (Figure 4) consisted of a cylinder closed off at one end by a piston that was operated by the pressure generator, and, at the other end, of a Pyrex-brand window placed in a window keeper. This allowed illumination of the cell contents by light from a borescope bulb and reflected off the face of the piston.

Cloud-point pressures at several temperatures were determined by raising the pressures until the complete clarification of the cell contents was attained. That point could usually be determined with a precision of ±0.5%. Darkening of the cell contents upon lowering the pressure was more gradual and less reproducible. The point of formation of a meniscus depended on both the nature of the sample and the rate of pressure decrease, as did the pressure differences between the point of clarification upon raising the pressure and the point of darkening that was readily visible to the naked eye upon lowering the pressure. The pressure at which the system clarified upon raising the pressure was therefore taken as the cloud-point pressure. The various sources of error which caused scattering of the cloud-point data, which was significantly greater than that expected from the precision of an individual measurement (see below), are unknown but may include a slow degradation of the molecular weight.

Because the highest pressure at which a meniscus first formed upon a small increase of the cell volume could not be well defined for all systems, and because this did not allow a precise measurement of the phase volumes at equilibrium, an accurate determination of the critical point on the basis of the careful extrapolation of liquid and gas volumes to their point of equality[4] was not attempted. Nonetheless, rough estimates of the critical conditions could be made.

III. Results

Figures 5, 6, and 7 show the cloud-point isopleths of the fractions 1482 and 1484 and of the whole polymer, respectively. (Only data points near the critical composition were taken for 1483). Note the nearly horizontal portion (slight negative slope), which is consistent with earlier data.[1] If these cloud-point isopleths were not intersected by their S–SCF branch, they would undergo a rapid descent toward a lower critical solution temperature lying on $(LV)_a$ somewhat below $C_a = C_1$, the first critical end point which, for a polymer solution, is effectively indistinguishable from the solvent's critical point (Figure 2). The sensitivity of the cloud-point

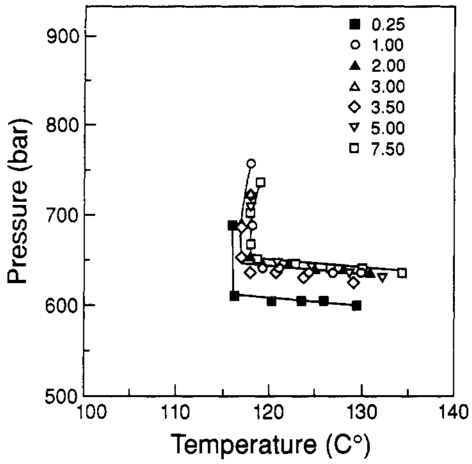

Figure 6. Cloud-point isopleths for fraction 1484.

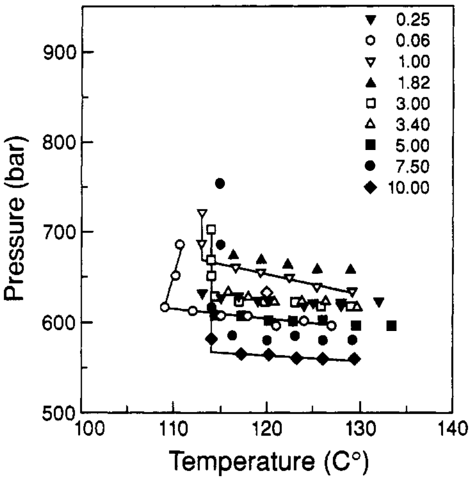

Figure 7. Cloud-point isopleths for HDPE 1.

pressure to molecular weight is also consistent with the earlier data and with the requirement that the critical value of the interaction parameter χ (or g)[5] must become larger as the molecular weight is reduced. The near-vertical sections of the isopleths, which represent S–SCF equilibrium, reflect their insensitivity to pressure (Figure 1). These data are not believed to be of sufficient accuracy to estimate the magnitude of $(\partial P/\partial T)_{\mathrm{coex}}$ or even its sign. A three-phase S–L–V equilibrium exists at the intersection of the two branches of each isopleth. Its direct observation would have been difficult with the present apparatus, and no such attempt was made.

Figure 8 represents the pressure vs composition or cloud-point curves (CPC) for the three samples at 125 °C and contains additional data points not measured as part of the isopleth study. These data allow a definition of the CPC for the dilute and moderately concentrated solutions. The scattering of the data is considerably greater than what would have been expected from the precision of individual cloud-point pressure measurement (see above). Molecular weight degradation of linear polyethylene during its characterization in trichlorobenzene by means of gel permeation chromatography was found to be a problem, even in the presence of antioxidants. The studies reported here were carried out in the absence of antioxidant.[8] While we do not believe that the location and shape of the CPC were affected strongly by polymer degradation, that process may have contributed to the observed scattering of the cloud-point pressure.

Estimates for the critical conditions at 125 °C, P_c and w_c (wt %), are as follows: for fraction 1482, P_c = 501 bar, w_c = 11.3%; for fraction 1483, P_c = 557 bar, w_c = 7.6%; for fraction 1484, P_c = 638 bar, w_c = 4.0%. The estimated location of the second critical end point, C_2, for the latter fraction is about 640 bar and 118 °C with w_c about 4%, but more uncertain than the temperature and pressure coordinates.

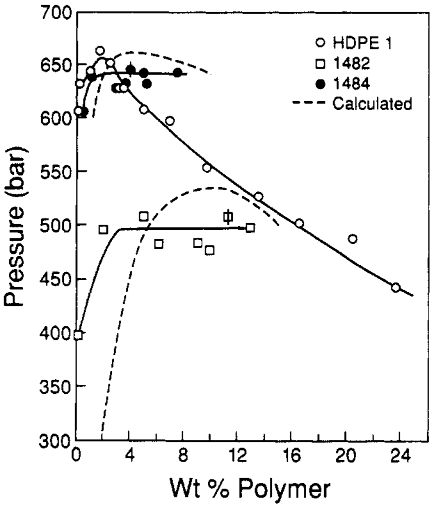

Figure 8. Cloud-point isotherms (CPC) at 125 °C. ф and ϕ mark approximate locations of critical points.

IV. Discussion

The data for linear and nearly linear polyethylene with propane reported here are consistent with earlier data on supercritical polyethylene–*n*-alkane systems[1] and encompass the region where fluid-phase equilibria (cloud points) impinge on solid–supercritical fluid equilibria. This region is entirely analogous to that described for low molecular weight organic solutes with supercritical solvents such as naphthalene–ethylene.[9]

The solubility of the polymer in the supercritical solvent becomes vanishingly small as the temperature is lowered below that of the second critical end point, C_2. Since the location of that point does, however, depend on the molecular weight of the polymer and its structure (branching), the region of S–SCF coexistence near C_2 is suitable for carrying out fractionation.[11,12]

Some comments on the calculation of the fluid-phase and the three-phase equilibria are appropriate. With the exception of suggesting the shape of the CPC, using the approach of de Loos et al.,[5] we do not attempt to calculate either the critical state or the cloud-point curve from an equation of state and a mixing function. The former calculation was first performed by Delmas and Patterson[13] based on Prigogine's equation of state and shown capable of predicting the critical states in polyethylene–*n*-alkane mixtures in a qualitative or at best semiquantitative fashion, but this and other approaches[14] based on reduced equations of state depend on as yet somewhat arbitrary choices of the characteristic (or reduction) parameters P^*, T^*, and V^* and are therefore not quantitatively successful. The more difficult problem of predicting binodals or cloud-point curves for supercritical polymer solutions was first approached by Bonner and co-workers[15,16] and later by de Loos and co-workers[5] for the system polyethylene–ethylene. The latter investigators based their calculations on the Koningsveld–Kleintjens[17] modification of the Flory–Huggins theory, which expresses the interaction energy, g, in terms of three parameters derived from an analysis of accurate critical data ($g = \alpha + \beta(P,T)/(1 - \gamma\phi)$, where ϕ is the volume fraction of polymer). Our experimental critical data are too few and not sufficiently accurate to allow this approach, and we attempted to obtain the parameter $\beta(P)$ at 125 °C from an analysis of the cloud-point curves themselves,[18] using the α and γ values found by de Loos et al. for polyethylene–ethylene.[5] We use this partly redundant method here merely to calculate the cloud-point curve of the two fractions from $\beta(P)$ determined for the whole polymer HDPE 1, whose cloud-point curve encompasses a wide pressure range (Figure 8). The only conclusion that can be drawn is that this seems to allow one to predict the approximate magnitude of the cloud-point pressure at its plateau, or the maximum pressure at which two fluid phases can coexist. The three-phase S–L–G equilibrium can be calculated, in principle, by combining information on the effects of pressure and dilution on the polymer's melting point with de Loos' approach, but our data are insufficient to give such calculations any predictive value.[19]

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