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Fluid Phase Equilibria in the System Polyethylene + Ethylene. 1. Systems of Linear Polyethylene + Ethylene at High Pressure

Theo W. de Loos,* Wim Poot, and George A. M. Diepen

Department of Chemistry, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands. Received February 5, 1982

ABSTRACT: In an optical high-pressure autoclave with sapphire windows and magnetic stirring, cloud point curves and critical curves in fluid systems of linear polyethylene + ethylene were measured in the temperature range 380–445 K and at pressures from 900 to 2000 bar for a number of polyethylene samples with known average molecular weights and known molecular weight distributions. It is found that an increase in molecular weight of the polyethylene causes a shift of the cloud point curve to higher pressures. The form of the cloud point curves and the position of the critical point are discussed in terms of model calculations by Šolc.

Introduction

The phase behavior of polyethylene + ethylene systems is of great importance for the industrial production of polyethylene.[1] Low-density polyethylene is synthesized under high pressure (1000–3000 bar) and at relatively high temperature (150–300 °C). In general, the reacting polyethylene + ethylene mixture must be kept in the homogenous fluid region. Since the conversion of ethylene is far from complete, the unreacted ethylene is separated from the polyethylene in a number of high-pressure separators at pressures of 150–350 bar. For the design of these separators information about the phase behavior of systems of polyethylene + ethylene is also needed.

It is well-known that the phase behavior of fluid polymer–solvent systems is strongly affected by the molecular weight[2,3] and by the molecular weight distribution[4,5] of the polymer and there are reasons to believe that also the degree of branching of the polymer plays an important role.[6] The existing experimental material[7–14] on fluid phase equilibria in systems of polethylene + ethylene only deals with the molecular weight dependence of the phase equilibria and it is only very recently that Luft and coworkers[12,19] presented cloud point curves and coexistence curves of polyethylene + ethylene systems using polymer samples with known molecular weight distribution.

For the development of a theory which makes it possible to predict fluid phase equilibria in systems of polyethylene + ethylene, it is necessary to have data available on systems with well-defined polyethylene samples.[6,20–23] In this paper we present experimentally determined cloud point curves and critical curves of a number of systems of linear polyethylene + ethylene. In subsequent papers we will give a thermodynamic analysis of these experimental results and present some data on systems of branched polyethylene + ethylene.

Experimental Section

1. **Equipment.** The measurements were carried out in an optical high-pressure cell designed for pressures up to 4000 bar and temperatures up to 450 K. This cell, which is provided with sapphire windows and magnetic stirring, is a modification of the one described by van Hest and Diepen.[24] For a detailed description of this apparatus and of experimental techniques, refer to ref 25.

The experimental setup is shown schematically in Figure 1. The pressure cell J is heated externally with two electric heating mantles K_1 and K_2, controlled by electronic regulators. To improve the temperature stability the pressure cell is submersed in a thermostated air bath L. In this way the temperature inside the autoclave can be maintained constant to better than 0.03 K. The temperature is measured with a platinum resistance thermometer I, which is placed in a shaft inserted in the pressure cell. The polyethylene + ethylene mixture, contained in a glass vessel,

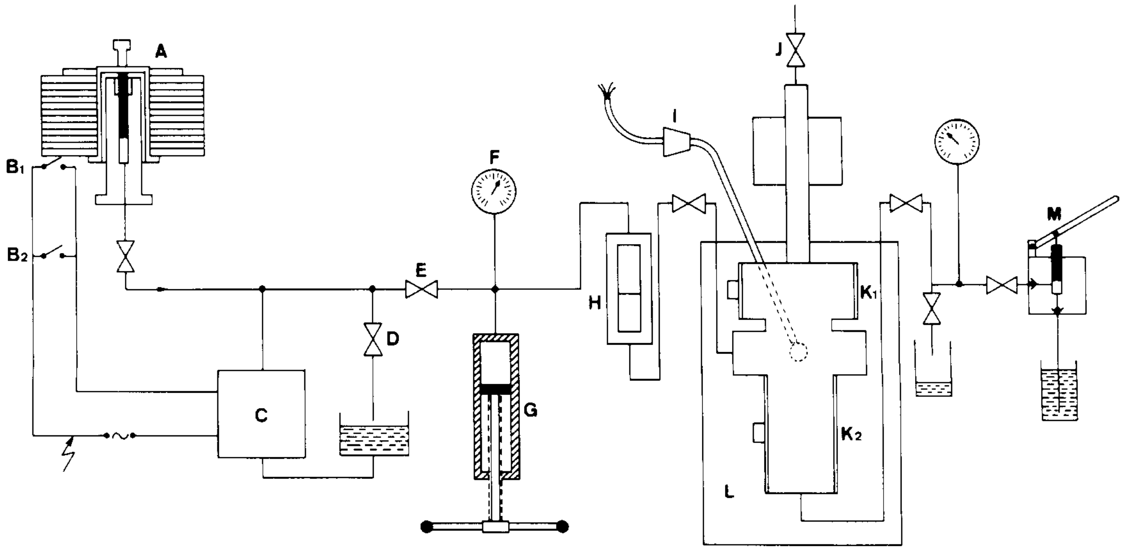

Figure 1. Experimental setup. Symbols are explained in the text.

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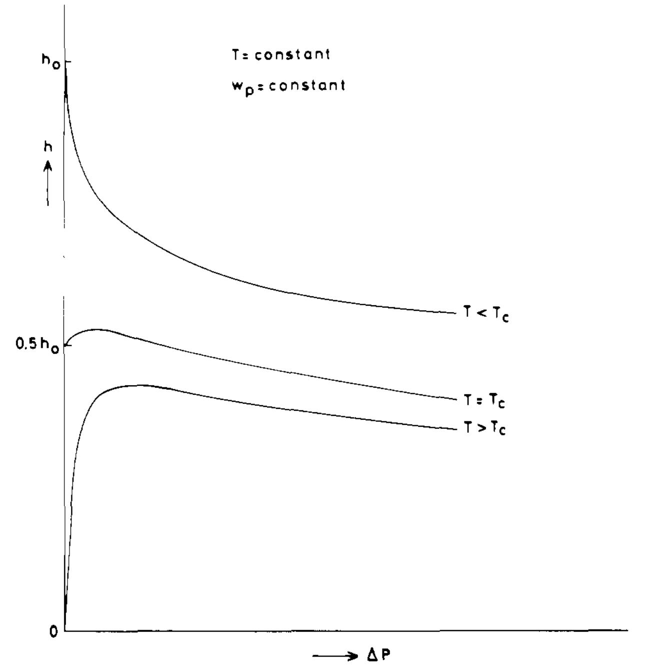

Figure 2. Schematic representation of the position of the phase boundary h at constant composition as a function of the pressure difference Δp between the cloud point pressure and the equilibrium pressure for a number of constant temperatures.

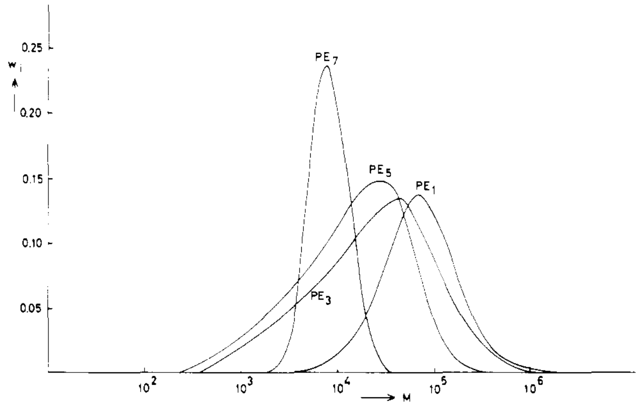

Figure 3. Molecular weight distribution $w_i(M_i)$ of the polyethylene samples PE1, PE3, PE5, and PE7 as found from gel permeation chromatography.

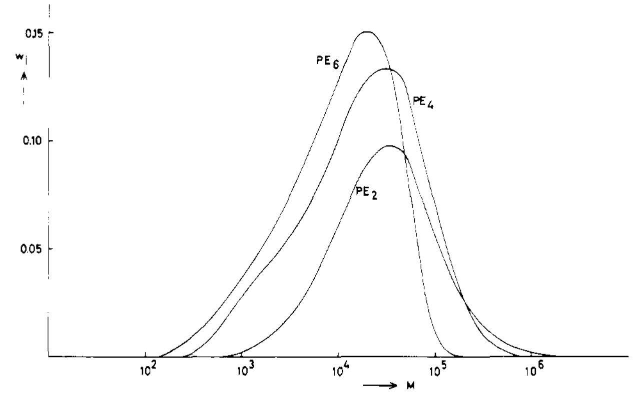

Figure 4. Molecular weight distribution $w_i(M_i)$ of the polyethylene samples PE2, PE4, and PE6 as found from gel permeation chromatography.

Table I

Molecular Characterization of the Polyethylene Samples

sample	$10^{-3}M_n$		$10^{-3}M_w$		$10^{-3}M_z$	
	A[a]	GPC[b]	A[a]	GPC[b]	A[a]	GPC[b]
PE1	43	56	118	99	231	185
PE2	20	30	58	58	148	191
PE3	8.6	10	55	52	300	163
PE4	12	8	53	50		150
PE5		7	42	37		100
PE6		5		21		39
PE7	7.6	7.6	9.2	8.8	10.5	10.4
PE8	3.0		3.7		4.3	

[a] M_n from osmometry, M_w from light scattering measurements, and M_z from ultracentrifugal measurements. [b] From gel permeation chromatography.

Table II

Critical Weight Fraction of Polymer $w_{p,c}$ for a Number of Systems of Linear Polyethylene + Ethylene in the Temperature Interval 403.15-443.15 K

system	$w_{p,c}$
PE1 + C_2H_4	0.069 ± 0.002
PE4 + C_2H_4	0.122 ± 0.002
PE5 + C_2H_4	0.135 ± 0.004
PE6 + C_2H_4	0.152 ± 0.002
PE7 + C_2H_4	0.162 ± 0.001
PE8 + C_2H_4	0.235 ± 0.005

is separated by mercury from the pressure-transmitting medium water. Pressure can be generated by hand pump M (up to 500 bar) or by high-pressure bench C, which is connected to the cell by means of the hydraulic oil-water separator H. Small changes in the pressure can be introduced with rotating pump G. The pressure balance A, which is accurate to ±1 bar, is used to measure to pressure.

The high-pressure bench C can be operated by hand with switch B_2 or automatically by the pressure balance (switch B_1). In the latter case the combination of the high-pressure bench and the pressure balance serves as a high-pressure manostat that maintains the pressure in the pressure cell constant within 0.1 bar.

2. Experimental Procedure. For an experiment with known composition of the polyethylene + ethylene mixture, the mixture was brought to conditions of temperature and pressure in the homogeneous-fluid region. Then the pressure was lowered slowly until the mixture started to become cloudy, which indicates the formation of a second fluid phase. Measurements of this so-called cloud point pressure at different temperatures give the cloud point isopleth (a p,T cross section for constant composition).

By observing the position of the phase boundary between the two phases, one can determine whether the observed phase separation is a bubble point (T less than the critical solution temperature T_c of that mixture) or a dew point ($T > T_c$). See Figure 2. In lowering the pressure at constant temperatures $T < T_c$, the position of the phase boundary moves downward in the measuring vessel. For temperatures $T > T_c$ the phase boundary appears at the cloud point pressure at the bottom of the vessel. With decreasing pressure the position of the phase boundary moves upward to a maximum height and goes down again. During the determination of the position of the phase boundary in the measuring vessel, it is important to be able to keep the pressure constant because the separation of the two phases takes a long time. To this aim the high-pressure manostat is used.

3. Materials. The mole fraction purity of the ethylene used was greater than 0.9998 (Matheson Gas Products) or 0.9995 (Phillips Petroleum Co.).

Table I gives the molecular characterization of the polyethylene samples used. Figures 3 and 4 give the molecular weight distribution of these samples found from gel permeation chromatography. For the polyethylene sample PE8 no molecular weight distribution is available. These samples have been put at our disposal by the Central Laboratory, DSM. For details concerning the preparation and characterization of the samples, the reader is referred to ref 26 and 27.

We added to the polyethylene + ethylene mixtures several parts

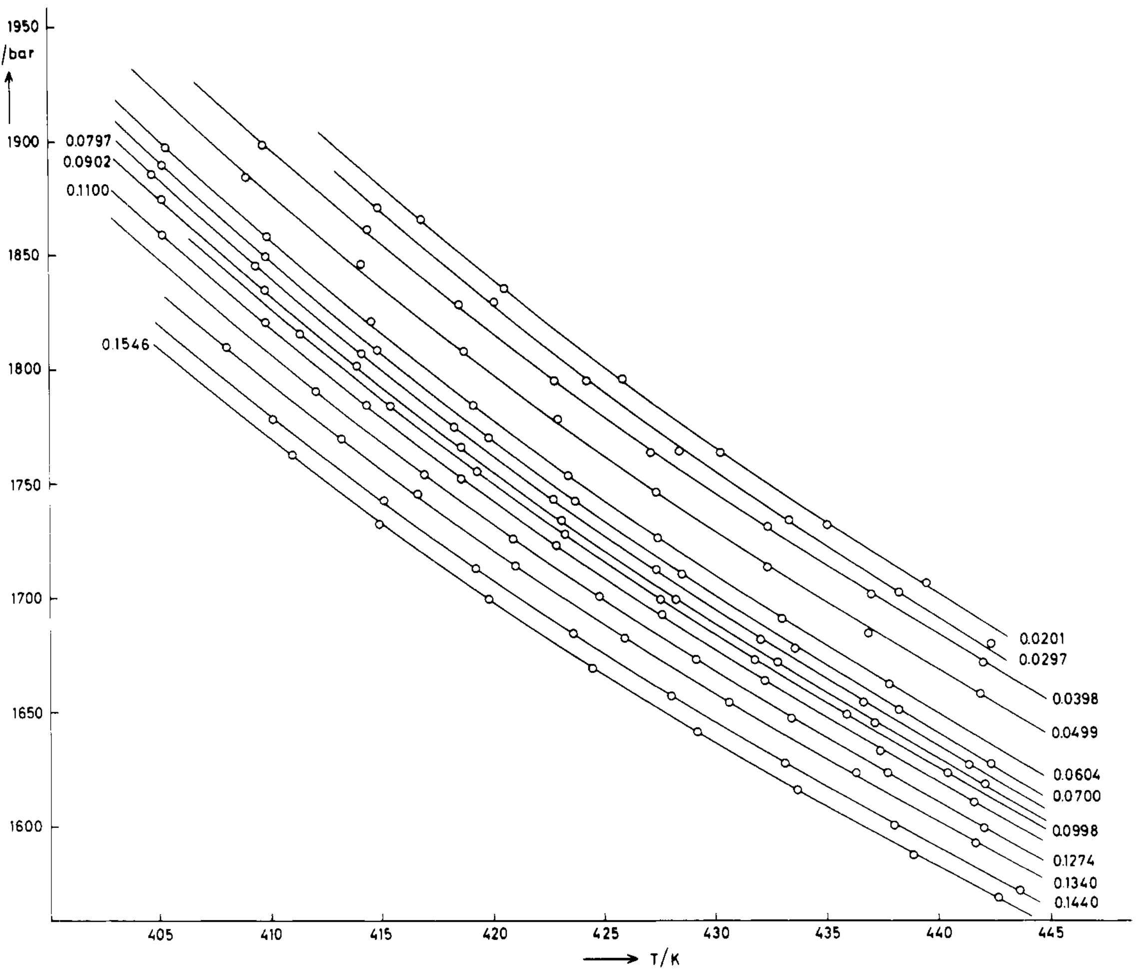

Figure 5. Cloud point isopleths in the system $[w_p{}^{PE1} + (1 - w_p)^{C_2H_4}]$ for indicated weight fractions w_p.

per million hydroquinone to suppress ethylene polymerization.

The error of the weight fraction polyethylene w_p in the polyethylene + ethylene mixtures is estimated to be ±0.0002 for $w_p = 0.004$ and ±0.0005 for $w_p = 0.300$.

Results

Some of the cloud point isopleths of the system PE1 + ethylene are shown in Figure 5. These isopleths form a bundle of almost parallel lines, a behavior that is observed in all the polyethylene + ethylene systems studied. dp/dT, the slope of the isopleths, is always negative and increases with increasing temperature. The reproducibility of the measured cloud point pressures was within 1 bar except at very low and very high values of the weight fraction polyethylene w_p. At low values of w_p, this is caused by the fact that at a pressure drop of 1 bar only a relatively small amount of the second phase is formed and that the appearance of the second phase is a bit retarded. At high values of w_p, the stirring of the polyethylene + ethylene mixture is less effective due to the higher viscosity of the mixture.

Figure 6 gives an example of the determination of the critical temperature T_c. In this figure the change in the position of the phase boundary as a function of pressure and at a number of constant temperatures is given for the system PE8 + ethylene at a number of different weight fractions of polyethylene. From this figure it can be seen that for $w_p = 0.2287$, 395.7 K $< T_c <$ 398.4 K, for $w_p = 0.2327$, 412.9 K $< T_c <$ 417.0 K, for $w_p = 0.2328$, 413.1 K $< T_c <$ 417.2 K, and for $w_p = 0.2351$, 430.7 K $< T_c <$ 434.8 K. A further reduction of the temperature interval between the dew point and the bubble point behavior is impossible because of the long-term temperature fluctuations inside the pressure cell.

For other polyethylene + ethylene systems the same behavior is found. The uncertainty in the critical temperature for a given composition is even higher for systems containing polyethylene with a higher molecular weight, because in these systems the determination of the position of the phase boundary takes much longer due to the higher viscosities of these systems. Despite this fact it is still possible to deduce the course of the critical curve from this type of measurements. See Figure 7, in which the T,w_p projection of the critical curves for the systems PE7 + ethylene and PE8 + ethylene are given. From this figure it can be concluded that the critical temperature rises with increasing weight fraction of the polymer, but the increase in critical weight fraction with increasing critical temperature is very small. So in view of the experimental uncertainties in the weight fraction and in the critical temperature, the critical weight fraction can be put constant in the temperature range investigated (403.15–443.15 K). This means that the critical curve coincides with one of the isopleths. In Table II the critical compositions $w_{p,c}$ for a number of polyethylene + ethylene systems are given.

Isothermal p,w_p cross sections (so-called cloud point curves) can be obtained from the p,T cross sections. For the system PE1 + ethylene such cross sections are shown in Figure 8. The p,x cross sections for the systems PE7 + ethylene and PE8 + ethylene are given in Figures 9 and

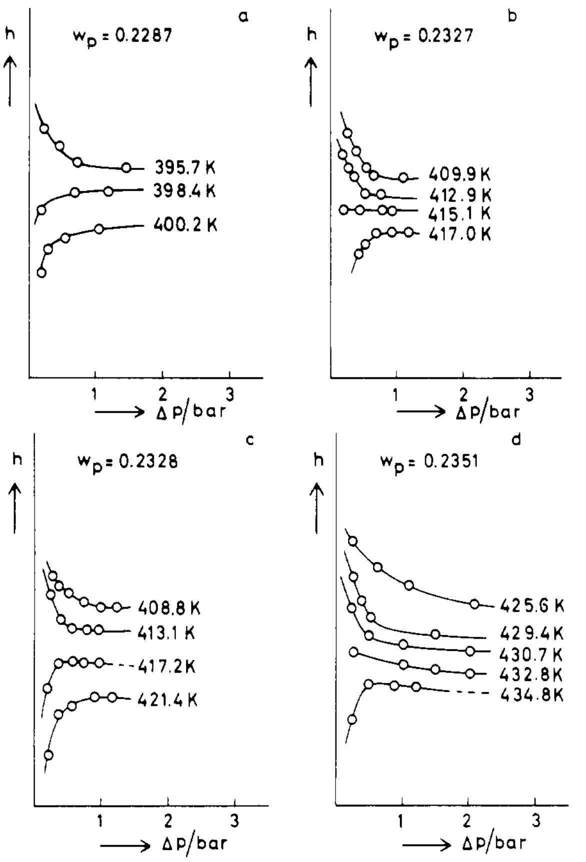

Figure 6. Experimental determination of the critical weight fraction of polymer $w_{p,c}$ in the system $[w_p^{PE8} + (1 - w_p)^{C_2H_4}]$: position of the phase boundary at constant values of w_p as a function of Δp, the pressure difference between the cloud point and the equilibrium pressure for a number of indicated temperatures.

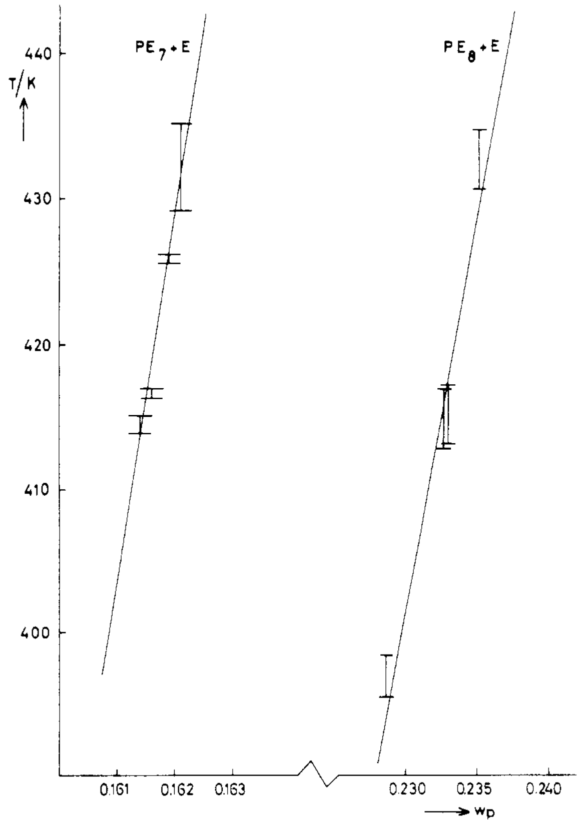

Figure 7. T,w_p projection of the critical curves of the systems PE7 + C_2H_4 and PE8 + C_2H_4. The uncertainties in T and w_p are indicated.

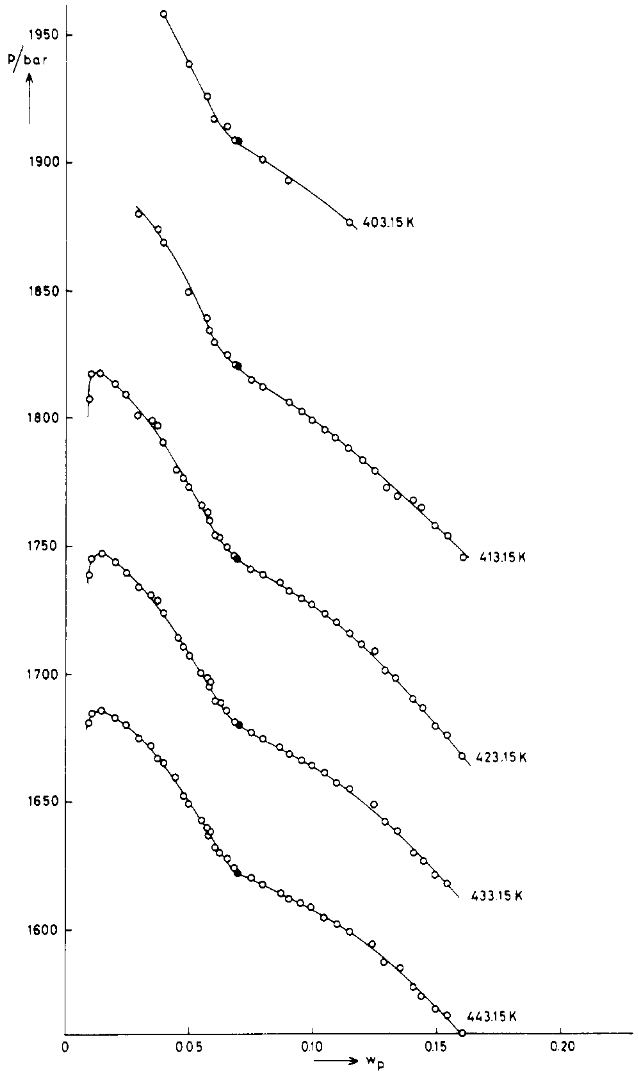

Figure 8. Cloud point curves in the system $[w_p^{PE1} + (1 - w_p)^{C_2H_4}]$: isothermal p,w_p cross sections for indicated temperatures. (●) Critical point.

10. In these figures the critical points are indicated. For the systems PE2 + ethylene and PE3 + ethylene only a few isopleths were measured. The corresponding p,x cross sections are given in Figures 11 and 12. Figure 13 gives the critical isopleths of the systems PE_4 + ethylene, PE5 + ethylene, and PE6 + ethylene.

Discussion

From Figures 8–10 one can see that the critical point is not found at the maximum of the cloud point curves but is always located at higher concentrations. This is caused by the polydispersity of the polymer. Model calculations by Šolc[28] show the influence of the molecular weight distribution of a polymer on the location of the critical point in systems of a homopolymer in a single solvent using the Flory–Huggins theory with a concentration-independent interaction parameter χ. Figure 14 shows the effect of the asymmetry of the molecular weight distribution. Normally, a situation as shown in Figure 14A is found. With increasing asymmetry of the molecular weight distribution, the cloud point curve appears to be broken at a concentration $w_{p,t} > w_{p,c}$, the critical concentration (Figure 14B). At this point an equilibrium between three fluid phases is found. The cloud point curve consists of two stable branches, connected by a metastable part, given by the dashed line. A further increase in asymmetry of the mo-

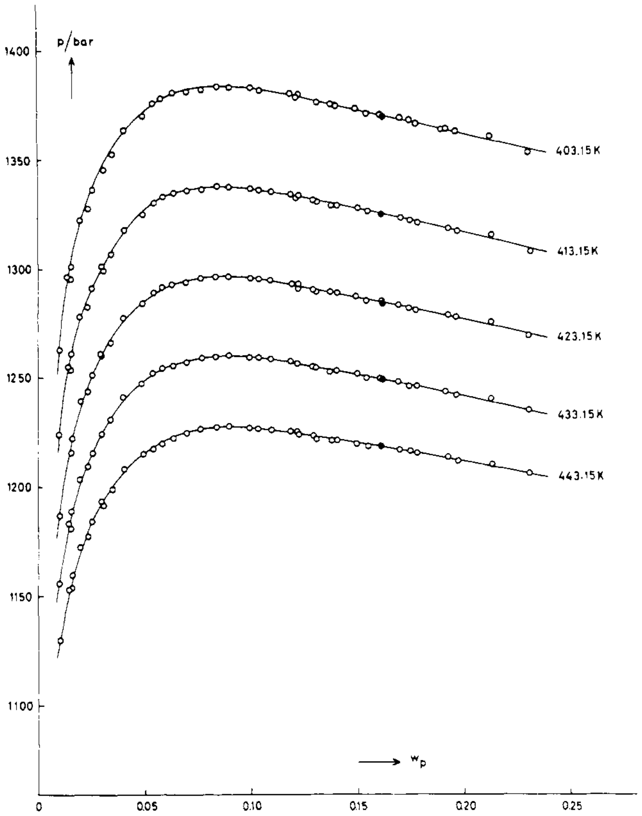

Figure 9. Cloud point curves in the system $[w_p^{PE7} + (1 - w_p)^{C_2H_4}]$: isothermal p,w_p cross sections for indicated temperatures. (●) Critical point.

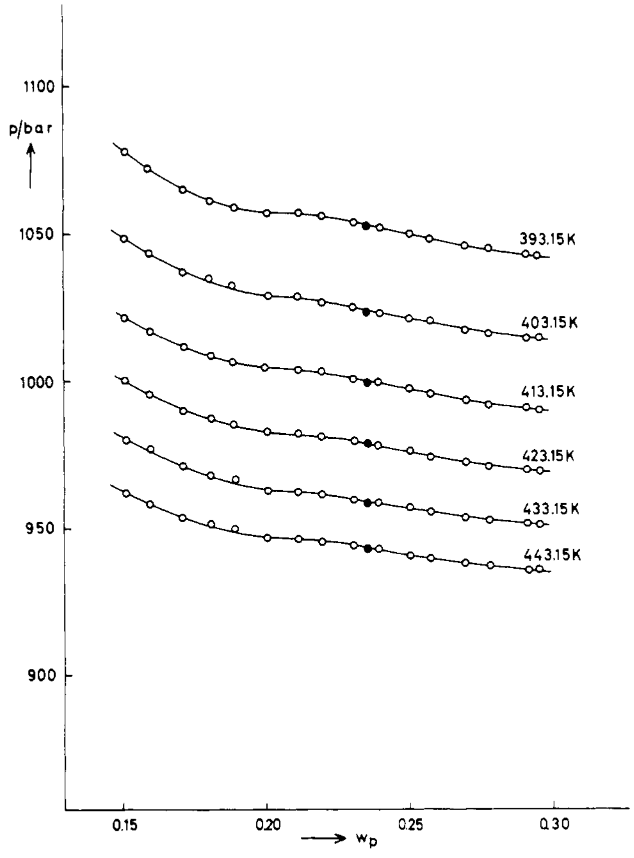

Figure 10. Cloud point curves of the system $[w_p^{PE8} + (1 - w_p)^{C_2H_4}]$: isothermal p,w_p cross sections for indicated temperatures. (●) Critical point.

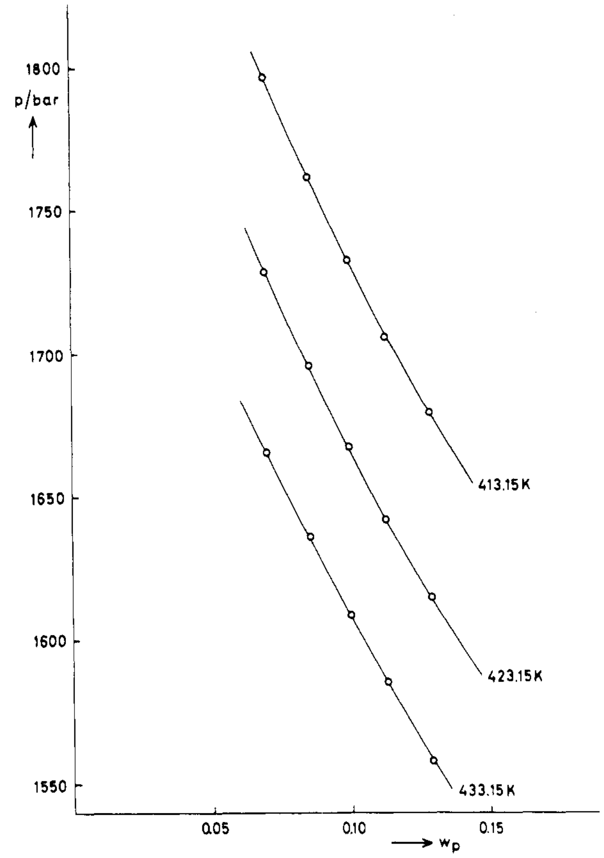

Figure 11. Cloud point curves of the system $[w_p^{PE2} + (1 - w_p)^{C_2H_4}]$: isothermal p,w_p cross sections for indicated temperatures.

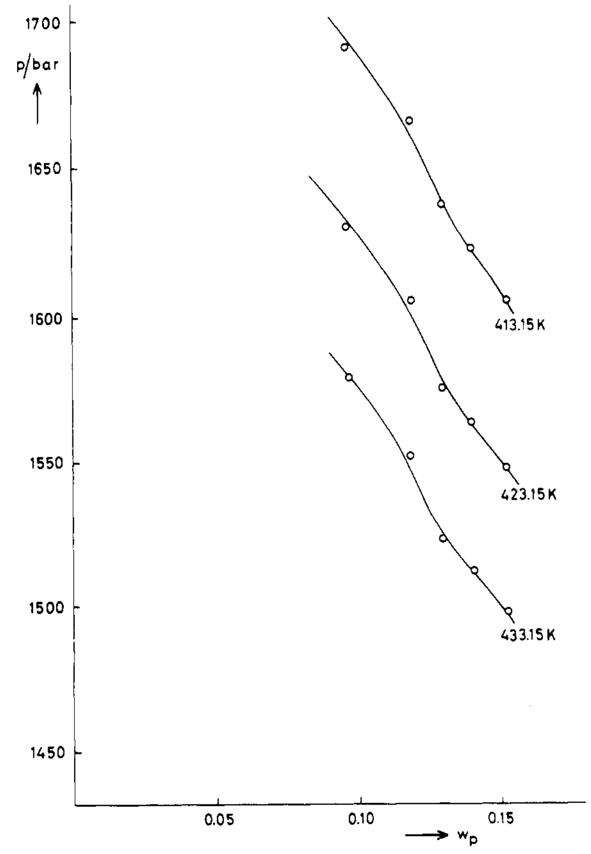

Figure 12. Cloud point curves of the system $[w_p^{PE3} + (1 - w_p)^{C_2H_4}]$: isothermal p,w_p cross sections for indicated temperatures.

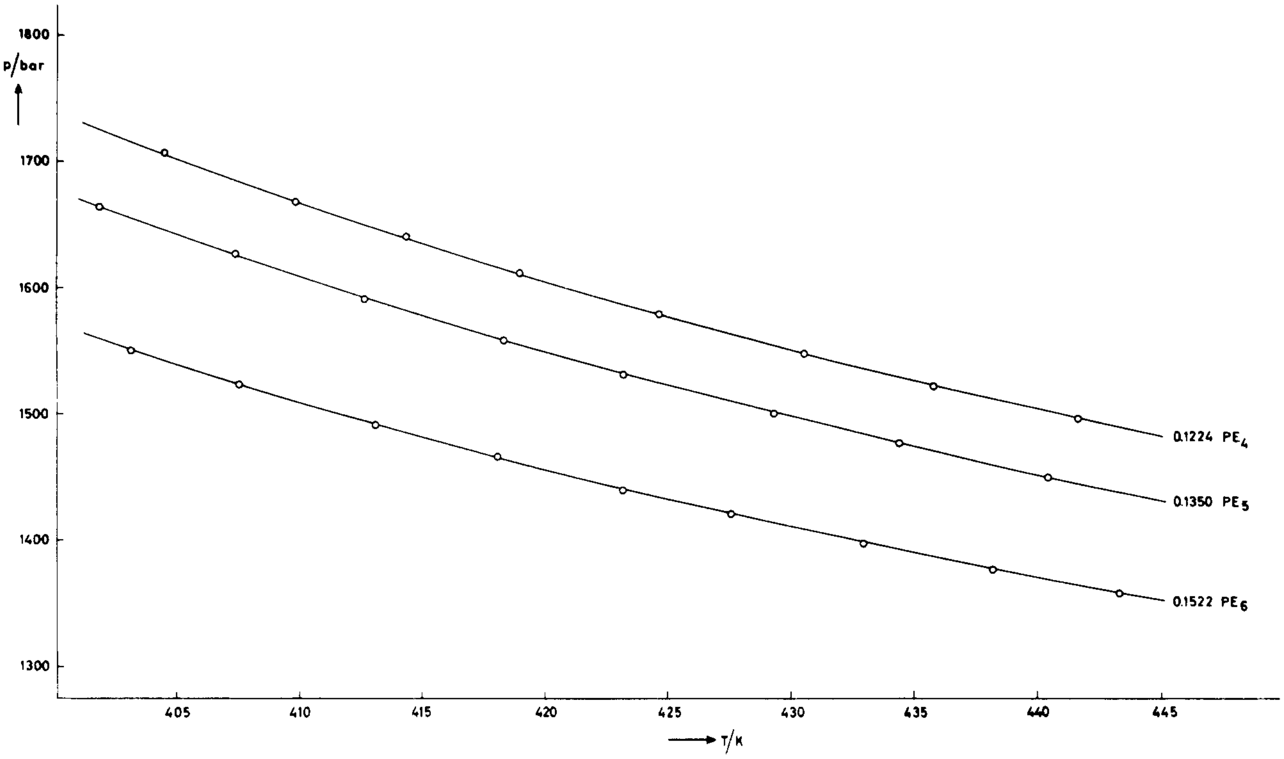

Figure 13. Cloud point isopleths in a number of $[w_p^{PE} + (1 - w_p)^{C_2H_4}]$ systems. The indicated weight fractions of polymer w_p practically coincide with the critical weight fraction of polymer $w_{p,c}$.

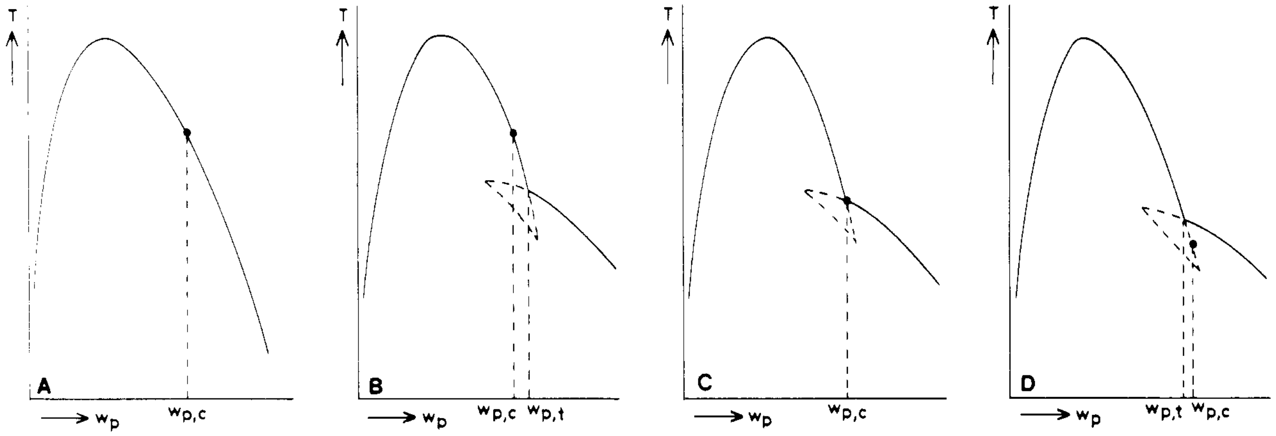

Figure 14. Effect of asymmetry of molecular weight distributions on the shape of the cloud point curve: (—) stable, (---) metastable, (●) critical point. After Šolc.[28]

lecular weight distribution causes a shift of the critical point to higher concentrations relative to the concentration of the three-phase point. Finally, $w_{p,c} > w_{p,t}$ and the critical point is metastable (Figure 14D). The cloud point curve of the system PE1 + ethylene (Figure 8) seems to be of the type of Figure 14B, the cloud point curve of the system PE7 + ethylene (Figure 9) corresponds to Figure 14A. In the system PE8 + ethylene (Figure 10) a stable critical point is found at a concentration $w_{p,c} > w_t$, although the depression in the cloud point curve is not very distinct. In terms of the calculations of Šolc this can be explained by a further shift of the critical point along the metastable part of the cloud point curve via the two singular points to concentrations higher than $w_{p,t}$. The average molecular weights of the polyethylene PE8 (Table I) give no reason to believe that this polyethylene sample has a very asymmetric molecular weight distribution, but Šolc used the Flory–Huggins equation with a concentration-independent χ. If the Flory–Huggins equation holds for the system polyethylene + ethylene, χ depends on composition.[29]

In Figure 15 the cloud point curves of five polyethylene + ethylene systems are given at $T = 423.15$ K. From this figure one can see that an increase in molecular weight of the polyethylene causes a shift of the cloud point curve to higher pressures. The same is found in systems of branched polyethylene + ethylene.[17-19] A direct comparison of systems with branched and linear polyethylene, however, is very difficult because the degree of branching has a marked influence on the cloud point pressure.[30]

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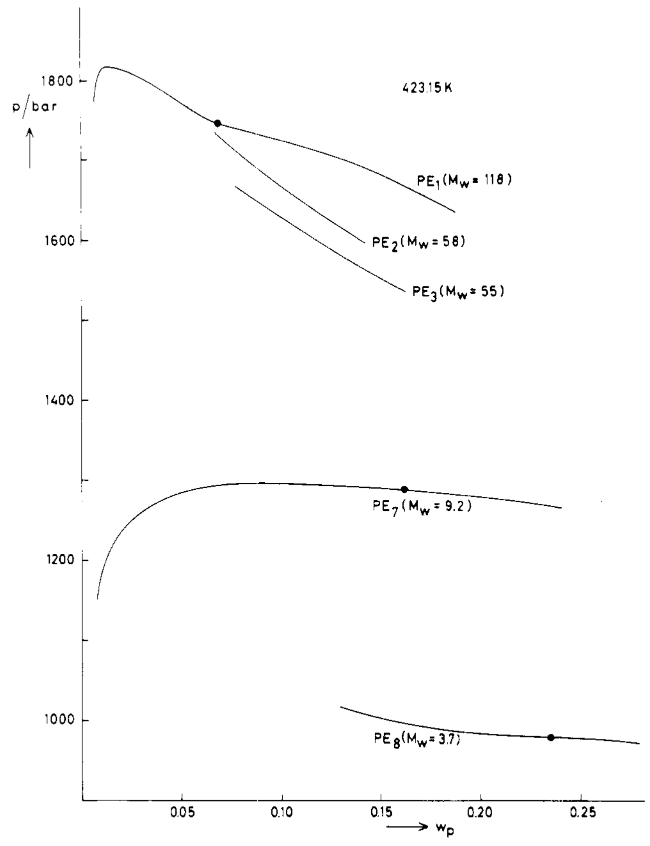

Figure 15. Cloud point curves of a number of $[w_p{}^{PE} + (1 - w_p)^{PE}]$ systems at $T = 423.15$ K showing the effect of the molecular weight of polyethylene (see Table I). (●) Critical point.

for putting the polyethylene samples at our disposal and to Dr. R. N. Lichtenthaler for constructive comments on the manuscript.

Registry No. Polyethylene, 9002-88-4; ethylene, 74-85-1.

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Fluid Phase Equilibria in the System Polyethylene + Ethylene. 2. Calculation of Cloud Point Curves for Systems of Linear Polyethylene + Ethylene

Theo W. de Loos,* Rüdiger N. Lichtenthaler, and George A. M. Diepen

Department of Chemistry, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands. *Received February 5, 1982*

ABSTRACT: The Flory–Huggins polymer solution theory as extended by Koningsveld and Kleintjens is used to calculate cloud point curves in systems of linear polyethylene + ethylene. To describe the effect of pressure we introduce an empirical pressure dependence in the interaction parameter. The adjustable parameters in this model are calculated from experimental critical loci, presented in the preceding paper. Attention is given to the effect of molecular weight distribution and to the algorithm for calculating the results. Calculated cloud point curves agree well with experimental cloud point curves, which were presented in the preceding paper for a number of linear polyethylene + ethylene systems.

Introduction

In a preceding paper[1] we reported experimentally determined cloud point curves and critical curves of a number of systems of linear polyethylene + ethylene. In this paper we show how the Flory–Huggins polymer solution theory[2,3] as extended by Koningsveld and Kleintjens[4] can be used to represent the cloud point curves of these systems. In these calculations the polydispersity of the polymer has to be taken into account. The adjustable parameters in the theory were obtained by fitting the experimentally determined critical curves. Due to the assumptions (e.g., rigid lattice model) made in deriving the Flory–Huggins theory, this theory and also its extension

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