

# Three and four phase predictions for polyethylene + hydrocarbon systems

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## Abstract

Experimental cloud-point isotherms for polyethylene + hydrocarbon systems can exhibit abrupt changes in slope when the polyethylene has a broad molar mass distribution. Equations of state with parameters correlated to qualitatively reproduce this behavior can result in cloud-point curves that fold, crossing themselves. The point of self-intersection is the terminus of a three-phase region, with three liquid-like phases in equilibrium. Teardrop-shaped three-phase boundaries have been calculated using the Modified Sanchez–Lacombe (MSL) equation of state for polyethylene + ethylene and polyethylene + *n*-hexane systems. We also show some examples of phase boundaries separating two-phase regions from three-phase regions, which exhibit folding and self-intersection, indicating the presence of a region with four liquid-like phases in equilibrium. A boundary isolating a four-phase region inside a three-phase region has been calculated for a polyethylene-*co*-octene-1 + *n*-hexane system. It has been noted that the polyethylene molar mass distribution, especially the extension to high molar masses, determines whether three-phase regions and four-phase regions occur.

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## 1. Introduction

Fluid-phase behavior for polyethylene and hydrocarbon mixtures is of interest to industrial solution polymerization processes. Solution polymerization reactors are typically operated to maintain a single homogenous phase. Multiple fluid phases could potentially lead to flow problems, as heavy components concentrate in a single phase, increasing the viscosity. In subsequent processing steps, the pressure of the mixture is reduced to separate the hydrocarbon solvent and residual ethylene from the polyethylene. Polyethylenes with broad molar mass distributions (MMD) can exhibit unusual phase transitions.

Experimental cloud-point isotherms can appear irregular for mixtures of broadly distributed polyethylenes and hy-

drocarbons, with changes from convex to concave curvature. Swelheim et al. [1] reported many cloud-point isotherms for a system of low-density polyethylene (LDPE) + ethylene that exhibit a noticeable wave across a range of polymer mass fractions. Spahl and Luft [2], in their experiments with another LDPE + ethylene system, identified the critical point as the point on the cloud-point isotherm where there is an abrupt change in slope. De Loos and co-workers found similar behavior in the cloud-point isotherms near the cloud point, critical for high-density polyethylene (HDPE) + ethylene systems [3,4] and LDPE + ethylene systems [5]. Mixtures with *n*-hexane exhibit similar curvature changes in the cloud-point isotherms at much lower pressures for HDPE + *n*-hexane [6,7] and polyethylene-*co*-octene-1 (PE-O also linear low-density polyethylene LLDPE) + *n*-hexane [8]. The experimental cloud-point wavy behavior was also observed for another HDPE + ethylene system [9]. The polyethylene in these experimental systems had varying degrees of polydispersity.

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At ambient pressure, three liquid-phase phenomena have been experimentally observed and also calculated from activity coefficient models. Koningsveld and Staverman measured three phases experimentally for a mixture of polyethylene and diphenyl ether [10]. Šolc [11,12] calculated cloud points using the Flory–Huggins approximation for polydisperse polymer + solvent systems showing cusps in the cloud-point lines where the cloud-point line crosses itself. He suggested that the calculated two-phase critical point could be located on the metastable part of the two-phase boundary located inside the liquid–liquid region. Kleintjens et al. [13] measured three liquid phases experimentally for a system of polystyrene + cyclohexane and were able to identify a three-phase region in their calculations. Šolc [14] later calculated three- and four-phase cloud points for hypothetical polymer + polymer mixtures.

In computations at high pressure, Koak and Heidemann [15] reported a folded isobar and a three-phase liquid–liquid–liquid point in computations with the Sanchez–Lacombe equation when correlating *n*-hexane, polyethylene cloud points. A metastable critical point was located inside the two-phase region. Jog et al. [16] calculated a self-intersection in a cloud-point line and inferred a three-phase point for a system of polyethylene-*co*-octene-1 (PE-O) + *n*-hexane [8] using the statistical associating fluid theory (SAFT).

The purpose of this paper is to examine three polyethylene + hydrocarbon systems that suggest the presence of a three-phase region. The first is the LDPE + ethylene system studied by Spahl and Luft [2]. They published a molar mass distribution for their LDPE sample, which has a low molar mass ( $M_w = 4.03$  kg/mol), a moderate polydispersity ratio ( $M_w/M_n = 3.58$ ), but a significant heavy molar mass tail. The second is a LDPE + ethylene system described by Swelheim et al. [1]. Their LDPE sample (DSM–Stamylan 3401) had a heavier molar mass ( $M_w = 250$  kg/mol) and a moderate polydispersity ratio ( $M_w/M_n = 10.9$ ). The third is the PE-*co*-octene + *n*-hexane system measured by de Loos et al. [8]. The PE-O sample is fairly heavy ( $M_w = 124$  kg/mol), with a moderate polydispersity ratio ( $M_w/M_n = 3.75$ ). Phase boundaries are calculated directly using an extension to three-phase and four-phase equilibria of the approach described by Koak and Heidemann [15]. Details will be given elsewhere.

## 2. The Modified Sanchez–Lacombe equation of state

The Modified Sanchez–Lacombe (MSL) equation of state incorporates two changes to the original Sanchez–Lacombe (SL) equation [17–19]. As was pointed out by Neau [20], the Helmholtz free energy expression in the original publications does not employ the ideal gas as the reference state. Neau proposed correcting this difficulty by deriving the residual Helmholtz free energy through the conventional integration of the pressure expression. A volume shift parameter is included to better represent liquid density [21].

The modified molar Helmholtz-free energy *A* is;

$$\frac{A - A^{ig}}{RT} = \frac{d}{b}(v_s - b) \ln \left( \frac{v_s - b}{v_s} \right) - \frac{a}{v_s RT} + d \quad (1)$$

The MSL pressure expression incorporates the shifted molar volume  $v_s$ .

$$\frac{P}{RT} = \frac{(1-d)}{v_s} - \frac{d}{b} \ln \left( \frac{v_s - b}{v_s} \right) - \frac{a}{v_s^2 RT} \quad (2)$$

The shifted molar volume  $v_s$  is equal to the sum of the molar volume  $v$  and the volume shift parameter  $c$  [21].

$$v_s = v + c \quad (3)$$

The composition dependent mixing parameters are combinations of pure component properties.

$$a = \sum_{i=1}^{n_c} \sum_{j=1}^{n_c} x_i x_j M_i M_j d_j \frac{v_i^* + v_j^*}{2} \sqrt{\varepsilon_i \varepsilon_j} (1 - k_{ij}) \quad (4)$$

$$b = \sum_{i=1}^{n_c} x_i M_i d_i v_i^* \quad (5)$$

$$c = \sum_{i=1}^{n_c} x_i M_i c_i \quad (6)$$

$$d = \sum_{i=1}^{n_c} x_i M_i d_i \quad (7)$$

The binary interaction parameter is assumed linearly dependent on temperature.

$$k_{ij} = k_{ij}^a + k_{ij}^b T \quad (8)$$

The Modified Sanchez–Lacombe equation requires four parameters for each pure component:  $\varepsilon_i$ ,  $v_i^*$ ,  $d_i$ , and  $c_i$ , and two parameters for each component pair:  $k_{ij}^a$  and  $k_{ij}^b$ . The notations for the parameters make use of some simplifications that are possible when no interaction parameters are included in the volume terms. The molar mass  $M_i$  has been factored out of the  $c_i$  and  $d_i$  parameters. All polymer components of a given type have the same  $c_i$  and  $d_i$  in this notation.

The solvent parameters were calculated using the SL parameterization of Gauter and Heidemann [21]. The critical properties and acentric factor were obtained from Reid et al. [22]. Parameters are summarized in Table 1. The pressure expression is the same for the Modified Sanchez–Lacombe equation and for the original form, hence the pure component parameters are interchangeable. Other parameters were correlated for each binary system based on three criteria:

Table 1  
Solvent properties from Reid et al. [22]

Description	Symbol	Ethylene	<i>n</i> -Hexane
Molar mass	$M$ (g/mol)	28.054	86.178
Critical temperature	$T_c$ (K)	282.4	507.5
Critical pressure	$P_c$ (bar)	50.4	30.1
Acentric factor	$\omega$ ( $T_r = 0.7$ )	0.089	0.299

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