

High pressure phase equilibria in the systems linear low density polyethylene + *n*-hexane and linear low density polyethylene + *n*-hexane + ethylene: Experimental results and modelling with the Sanchez-Lacombe equation of state

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Abstract

Cloud point isopleths, bubble-point isopleths and liquid–liquid–vapour bubble point isopleths were measured for a binary system of linear low density polyethylene (LLDPE) and *n*-hexane and for the ternary system LLDPE + *n*-hexane + ethylene. The experiments were performed according to the synthetic method in the temperature range 400–500 K and at pressures up to 14 MPa. The LLDPE used was a hydrogenated polybutadiene and was almost monodisperse ($M_w/M_n = 1.19$). Measured experimental data for the system LLDPE + *n*-hexane and experimental data for the system LLDPE + ethylene taken from literature [H. Trumpf, Th.W. de Loos, R.A. Krenz, R.A. Heidemann, High pressure phase equilibria in the system linear low density polyethylene + ethylene: experimental results and modeling, *J. Supercrit. Fluids* 27 (2003) 205–214.] were modelled with the modified Sanchez-Lacombe equation of state. The same LLDPE sample was used in both experiments. The parameters for LLDPE were found by performing a sequence of non-linear regressions on pressure–volume–temperature reference data for molten polyethylene and the experimental cloud point data for the systems LLDPE + *n*-hexane and LLDPE + ethylene. From this information and a Sanchez-Lacombe fit to *n*-hexane + ethylene data the phase behaviour of the ternary system LLDPE + *n*-hexane + ethylene can be predicted. Using this procedure the influence of the ethylene concentration on the cloud point pressure is slightly under predicted. Therefore, the LLDPE–ethylene binary interaction parameter was adjusted to ternary LLDPE + hexane + ethylene cloud point data. In this way the modified Sanchez-Lacombe equation gives a very good description of the ternary cloud point curves and an almost quantitative prediction of the ternary bubble point and liquid–liquid–vapour boundary curves.

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1. Introduction

LLDPE is produced by solution copolymerization of ethylene and a 1-alkene in a hydrocarbon solvent. This reaction is commonly performed in the one-phase fluid region where the polymer and the monomers are dissolved in the solvent. For this, the pressure must be high enough to keep the reaction mixture in a single phase at the reaction temperature. The

low-temperature boundary of the one-phase fluid region is determined by the solidification of the LLDPE. The high-temperature boundary, the cloud point curve, is determined by the onset of a liquid–liquid phase split, characterized by a lower critical solution temperature (LCST). For some process variants also the location of the liquid–liquid–vapour boundary is of importance for the separation step.

Kennis et al. [1] showed that the addition of nitrogen to a polyethylene + *n*-hexane system lowers the solvent power for the polymer and shifts the LCST to lower temperatures and higher pressures. This means that the supercritical gas acts as an anti-solvent. Similar effects in other polymer + solvent systems

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with other low molecular weight supercritical fluids have been found [2–6]. de Loos et al. [4] studied the phase behaviour of different LLDPE samples with *n*-hexane, *n*-heptane, *n*-octane, cyclohexane and 2-methyl-pentane. For these systems LCST-type phase behaviour was also found. These authors showed that the addition of ethylene to a solution of 10 wt.% poly(ethylene-co-1-octene) in *n*-heptane lowers the lower solution temperature (cloud point) with approximately 14 K/wt.% ethylene added.

Various equations of state have been proposed and modified to predict polymer–solvent phase behaviour. Jog et al. [7] used the SAFT equation of state [8] to describe the phase behaviour of the LLDPE + solvent systems investigated by de Loos et al. [4]. The same equation of state was used by ter Horst et al. [6] to model the influence of the addition of supercritical gases on the phase behaviour of systems of polyethylene + cyclohexane and polystyrene + cyclohexane. The Sanchez-Lacombe equation of state [9,10], which is used in this work, was used by Gauter and Heidemann [11] to model the phase behaviour of the systems polyethylene + *n*-hexane and polyethylene + ethylene. Trumpi et al. [12] used the Sanchez-Lacombe equation of state to describe the phase behaviour of a LLDPE + ethylene system. The Sanchez-Lacombe equation was used in the modeling reported in this manuscript because it is amongst the simplest of the equations that accounts for large differences in molecular chain lengths and because of its successful use in the cited manuscripts.

In this paper, experimental cloud point data and bubble point data are presented for mixtures of an LLDPE + *n*-hexane or *n*-hexane + ethylene, using the same LLDPE sample that was used by Trumpi et al. [12] to study the phase behaviour of LLDPE + ethylene. The experimental data on these binary LLDPE systems have been fitted using the modified Sanchez-Lacombe equation of state. In the data fitting, the parameters for the polyethylene and a temperature dependent interaction parameter have been adjusted. Additional data on the system *n*-hexane + ethylene were fitted to obtain the binary interaction parameter of this binary subsystem. The resulting parameters are used to predict the influence of the addition of ethylene on the phase behaviour of LLDPE + *n*-hexane.

2. Experimental

The hexane used had a minimum purity of 99.5% (Fluka puriss p.a.) and was stored over molecular sieve to remove traces of water. The mole fraction purity of the ethylene was greater than 0.9998 (Matheson Gas Products). The polyethylene sample was a hydrogenated polybutadiene (PBD 50000) that was made by DSM and is regarded as a linear low-density polyethylene (LLDPE). The number-average molar mass is $M_n = 43,700$ g/mol, $M_w/M_n = 1.19$ and the branch density is 2.05 methyl groups per 100 carbons on the main chain. Slightly different average molar masses were reported for this same polymer in ref. [12]. The SEC chromatogram for the polymer, which is shown in Fig. 1, was digitized and re-analyzed in this study. Since the differences are small, no effort was made to force exact agreement between the two sets of values. Additional

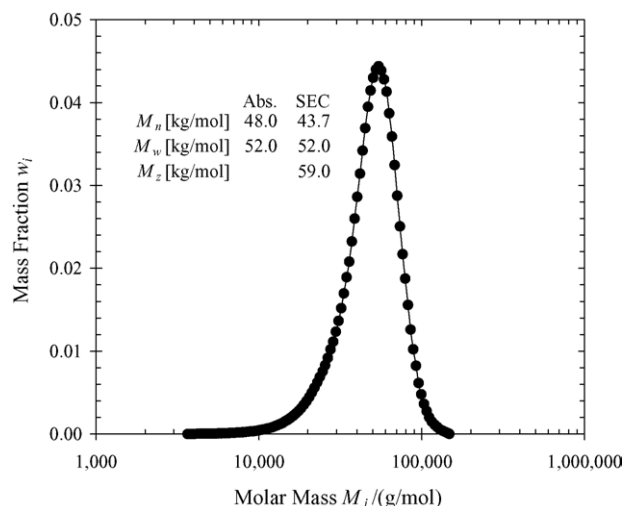


Fig. 1. SEC distribution of the polyethylene sample used: (●) pseudo-components.

molecular characterization of the LLDPE sample appears in Table 1.

The experiments were carried out using the so-called Cailletet apparatus according to the synthetic method. A detailed description of the apparatus and the experimental procedure is given elsewhere [13]. A sample of the mixture with known composition is confined over mercury in a narrow glass tube, mounted in a thermostatic bath. At constant temperature cloud points, vapour–liquid bubble points and vapour–liquid–liquid bubble points were measured visually by adjusting the pressure. During the experiments the temperature is maintained constant to within 0.1 K. Critical points for the system LLDPE + *n*-hexane were measured using a method described in literature [14].

The temperature is measured with a Pt100 resistance thermometer, which was calibrated against a standard thermometer with an accuracy of ± 0.01 K. The uncertainty in the measured temperature was approximately 0.02 K. The pressure is applied hydraulically and is measured with a dead weight pressure gauge (De Wit, accuracy ± 0.005 MPa). The uncertainty in the experimental bubble-point pressures is 0.01 MPa and in the cloud-point pressure 0.02 MPa.

The amounts of LLDPE and *n*-hexane added to the sample cell are determined by weight. LLDPE and *n*-hexane are degassed under vacuum using a freeze–thaw technique. Ethylene is added volumetrically. A detailed description of the sample preparation and gas filling apparatus has been given by de Loos [15].

Table 1
Molecular characterization of LLDPE

	Absolute ^a	SEC ^b
M_n (g/mol)	48,000	43,700
M_w (g/mol)	52,000	52,000
M_z (g/mol)	–	59,000
BD (CH ₃ /100C)	2.05	–

^a M_n from osmometry, M_w from light scattering measurements.

^b M_n , M_w , and M_z , from size exclusion chromatography.

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