THE INFLUENCE OF THE ADDITION OF SUPERCRITICAL ETHYLENE ON THE HIGH PRESSURE PHASE BEHAVIOUR OF THE SYSTEM LINEAR LOW DENSITY POLYETHYLENE + n-HEXANE: EXPERIMENTAL RESULTS AND MODELLING WITH THE SANCHEZ-LACOMBE EOS

Th. W. de Loos[*]**, I. Nagy**
Department of Chemical Technology, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands
R.A. Krenz, R.A. Heidemann
Department of Chemical and Petroleum Engineering, University of Calgary, 2500 University Drive NW, Alberta T2N 1N4, Canada

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Cloud point isopleths, liquid-vapour 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 to 500 K and at pressures up to 14 MPa. The LLDPE used was a hydrogenated polybutadiene and was almost monodisperse (M_w/M_n = 1.18). Measured experimental data for the system LLDPE + n-hexane and experimental data for the system LLDPE + ethylene taken from literature [Trumpi et al., J. Supercrit. Fluids, Vol. 27, **2003**, p. 205] 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 the experimental cloud-point data for the systems LLDPE + n-hexane and LLDPE + ethylene and pressure-volume-temperature reference data for molten polyethylene. From this information and a Sanchez-Lacombe fit to n-hexane + ethylene data the phase behaviour of the ternary system LLDPE + n-hexane + ethylene is predicted. It is found that the modified Sanchez-Lacombe equation gives a very good prediction of the ternary bubble-point curves and liquid-liquid-vapour boundary curves. The prediction of the influence of the ethylene concentration on the cloud point pressure is slightly under predicted.

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 dissolve the ethylene. 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 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 also LCST-type phase behaviour 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 per 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.

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. to study the phase behaviour of LLDPE + ethylene [12]. 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.

MATERIALS AND METHODS

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 $M_n = 43,400$ g/mol, $M_w/M_n = 1.18$ and the branch density is 2.05 methyl groups per 100 carbons on the main chain. In Figure 1 a discretization of the GPC curve for this sample is presented.

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, dew 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]
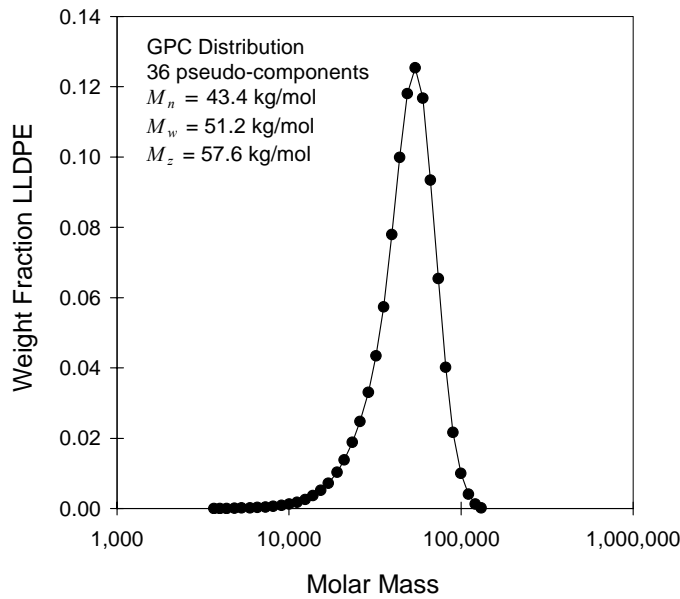
Figure 1 : GPC distribution of the LLDPE sample used.

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 LDDPE 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].
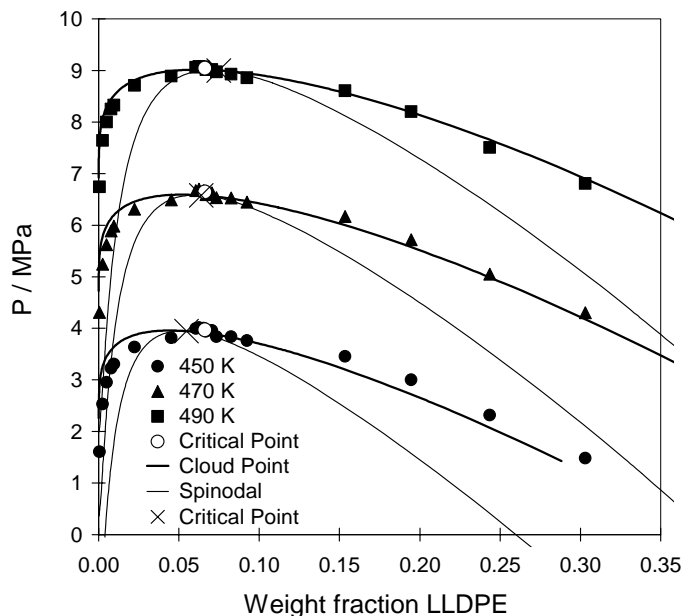

Figure 2 : Isothermal cloud point curves of LLDPE + n-hexane Symbols: experiments; curves: modified Sanchez-Lacombe fit.

EXPERIMENTAL RESULTS

From the experimental cloud point isopleths for the system LLDPE + n-hexane isothermal cloud point curves at 450, 470 and 490 K were obtained by interpolation. These data are plotted in Figure 2. The critical weight fraction of LLDPE was found to be (0.0666 ± 0.0012). Within the experimental uncertainty no change of the critical weight fraction with temperature could be found in the temperature range investigated. The critical points do not coincide with the pressure maxima of the cloud point isotherms as a result of the polydispersity of the polymer. The critical pressure increases with increasing temperature and the system shows lower critical solution temperatures.

Figure 3 shows the influence of the addition of ethylene on the phase behaviour of LLDPE + n-hexane. In this figure the LLDPE weight fraction is approximately constant at 0.05 and the ethylene weight fraction varies from 0 to 0.03. The figure shows that the addition of ethylene to LLDPE + n-hexane shifts the cloud point temperature to lower temperatures and higher pressures (10 K or 3 MPa per wt% ethylene). With increasing ethylene concentration also the liquid-vapour and the liquid-liquid-vapour bubble-point pressure increases.
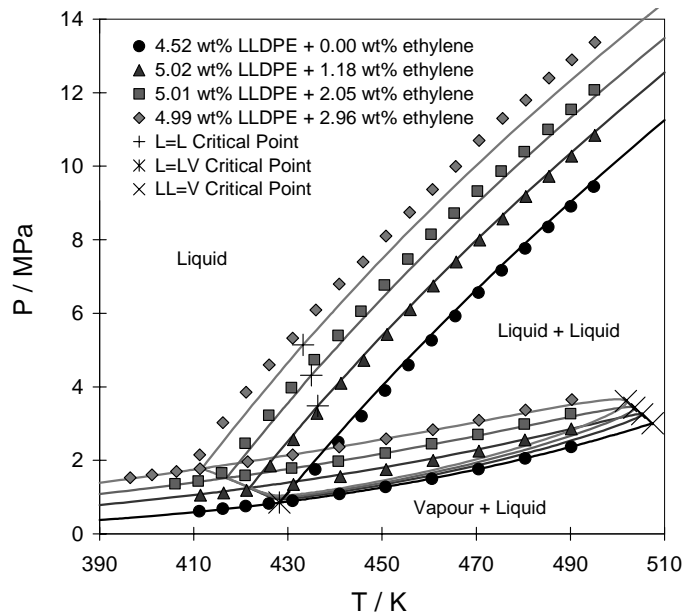
Figure 3 : Phase behaviour of LLDPE + n-hexane + ethylene: influence of the addition of ethylene at LLDPE weight fraction of 0.05. Symbols: experiments; curves: Sanchez-Lacombe predictions

MODELLING

Polymer Characterization

The LLDPE sample used in the experiment is nearly monodisperse (M_w/M_n = 1.18). For the purpose of modelling, 36 pseudo-components, indicated by the symbols in Figure 1, were generated from the GPC distribution using the anchored quadrature method.

The Modified Sanchez-Lacombe Equation

The original Sanchez-Lacombe equation had three pure component parameters [9,10]: ε_i, the attractive energy parameter, v_i^*, the volume occupied per mole of lattice sites, and d_i, the number of lattice sites per molecule. In this work the modified Sanchez-Lacombe equation of Neau [16] is used. The Sanchez-Lacombe parameters for n-hexane and ethylene were calculated from the pure component critical properties using the proposal of Gauter and Heidemann [17]. For a polymer, the number of lattice sites per molecule is proportional to the molar mass; i.e., $d_i = M_i d_p$. Gauter and Heidemann [11] proposed including a volume shift parameter, c_i, similar to that suggested by Péneloux et al. [18] to provide some freedom in matching polymer-solvent equilibrium data while retaining a good fit of PVT reference data for the molten polymer. In fitting simultaneous of the phase equilibrium data for LLDPE + n-hexane and the literature cloud point data for LLDPE + ethylene [12], the polymer energy parameter ε_p was regarded as variable. For a fixed value of ε_p, the three remaining polymer parameters, v_p^*, d_p and c_p were found through a non-linear least squares fit of the reference PVT data of Olabisi and Simha [19] for liquid low density polyethylene (LDPE). Linear low density polyethylene (LLDPE) is assumed to exhibit similar PVT behaviour to low density polyethylene (LDPE).

The binary interaction parameter between any two species was regarded as temperature dependent, in the form;

$$k_{ij} = k_{ij}^a + k_{ij}^b T \tag{1}$$

Six parameters were available to fit the data for a single polymer + solvent system. For the chosen value of ε_p the pure polymer parameters v_p^*, d_p, and c_p parameters were fit to the LDPE PVT data and the binary parameters, k_{ij}^a and k_{ij}^b were fit to the cloud point data for a binary polymer + solvent system. The entire procedure is repeated by varying ε_p until a good fit of both binary systems (LLDPE + ethylene and LLDPE + n-hexane) is achieved.

Modelling Results

The resulting Sanchez-Lacombe parameters for LLDPE are summarized in Table 1. The Sanchez-Lacombe model provides a good fit of the two polymer solvent systems over the entire range of compositions, temperatures and pressures. The AAD of calculated and experimental cloud point temperatures for LLDPE + n-hexane is 1.44 K and LLDPE + ethylene 1.54 K. The calculated results for LLDPE + n-hexane at 450, 470 and 490 K are plotted in Figure 2.

The critical polymer mass fractions for LLDPE + n-hexane predicted by the Sanchez-Lacombe model varies from 0.0547 at 450 K to 0.0748 at 490 K. Experimentally the critical LLDPE mass fractions in this temperature range was found at (0.0666 ± 0.0012). No trend with temperature was observed.

The LLDPE energy parameter, $\varepsilon_p = 4.014$ kJ/mol, is of the same magnitude as those reported for LDPE for the original SL equation by Gauter and Heidemann [11] ($\varepsilon_p = 4.65$ kJ/mol and 4.900 kJ/mol).

Table 1 : Modified Sanchez-Lacombe parameters for LLDPE

energy parameter	ε_p	4.014	kJ/mol
volume occupied per lattice site	$v_p{}^*$	8.405	cm^3/mol
number of lattice sites occupied	d_p/M_i	0.06983	mol/g
volume shift parameter	c_p/M_i	-0.5066	cm^3/g

binary interaction parameter for n-hexane + ethylene k_{ij} = -0.1520 + 0.0004405T

binary interaction parameter for LLDPE + ethylene k_{ij} = 0.02897 – 0.00008241T

binary interaction parameter for LLDPE + n-hexane k_{ij} = -0.1953 + 0.0003880T

In Figure 3 the modified Sanchez-Lacombe predictions for the ternary system LLDPE + n-hexane + ethylene are plotted. The results of the calculations show that the influence of the ethylene concentration on the cloud point pressure is slightly under predicted, while the modified Sanchez-Lacombe model gives a very good prediction of the influence of the ethylene concentration on the vapour-liquid and liquid-liquid-vapour bubble point curves.

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