



Prediction of the liquid–liquid phase equilibria for polydisperse polyethylene solutions under conditions of high temperature and pressure



Masashi Haruki^{*}, Kotaro Adachi, Shohei Fujikawa, Shin-ichi Kihara, Shigeki Takishima^{**}

Department of Chemical Engineering, Graduate School of Engineering, Hiroshima University, 141, Kagamiyama, Higashi-Hiroshima, 739-8527, Japan

ARTICLE INFO

Article history:

Received 9 December 2015

Accepted 9 December 2015

Available online 25 December 2015

Keywords:

Polydisperse polyethylene solution

Phase equilibrium

Phase boundary pressure

Molecular weight distribution

Sanchez–Lacombe equation of state

ABSTRACT

In the present study, the liquid–liquid (LL) phase equilibria for the hexane + polydisperse polyethylene (PE) and the ethylene + hexane + polydisperse PE systems were simulated using the Sanchez–Lacombe equation of state, in order to investigate the effects of the addition of ethylene and the polydispersity of PE on the LL phase equilibria of the PE solution. In the calculation, the polydispersity of PE was represented as a mixture of 16 types of monodisperse PE. The interaction parameter between hexane and PE was determined by fitting to the LL phase boundary curve of the hexane + polydisperse PE binary system in the previous work, and it depended on the molecular weight of PE. The interaction parameter between ethylene and PE was used, as also determined from the LL phase boundaries for the ethylene + hexane + polydisperse PE system in the present work. And, the parameter of the ethylene–hexane pair that was based on the value reported in the literature was used.

The simulated results indicated that the critical PE weight fraction increased as the feed ethylene content increased. On the other hand, although the addition of ethylene greatly increased the LL phase boundary, the ethylene content had only a small influence on the PE content of both separated LL phases and their molecular weight distributions for the LL phase equilibria. The effect of the polydispersity of PE was notable on the PE weight fractions in the separated phases.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Polyethylene (PE) is one of the most utilized polymers, and is used for a variety of commodities such as wrapping materials. During the PE production process, many types of olefin comonomers are added to enhance the functionality of PE. Among the polymerization methods, solution polymerization at high temperature and pressure has become a standard method for the easy addition of comonomers. For the process design and operation of a reactor and separator, a knowledge of the liquid–liquid (LL) phase boundary for the ethylene (monomer of PE) + comonomer + solvent + PE system is important, and many experimental and theoretical studies have reported the LL

phase boundaries of this system [1–11]. Many polydisperse PEs are industrially produced. When PE has polydispersity, the LL phase boundary curve and the LL phase equilibrium curve are not in accord, even in a solvent + PE binary system [12]. Therefore, the LL phase equilibria for PE solutions at high temperature and pressure are indispensable data. However, the available studies on the LL phase equilibria of PE solutions are quite limited.

In our previous work [13], the LL phase equilibria for a hexane + polydisperse PE system were experimentally measured at 473 K, and both the compositions and molecular weight distributions (MWDs) of the PE-rich and the hexane-rich phases were determined. Moreover, the LL phase boundary at 473 K that was also measured in the previous work was correlated using the Sanchez–Lacombe equation of state (S-L EOS), wherein the interaction parameter between hexane and PE was determined, and the characteristic parameter, ρ^* , of PE was also determined in order to express the critical point at 473 K as well as the LL phase boundary

^{*} Corresponding author.

^{**} Corresponding author.

E-mail addresses: mharuki@hiroshima-u.ac.jp (M. Haruki), r736735@hiroshima-u.ac.jp (S. Takishima).

curve. The predictions of the LL phase equilibria were subsequently carried out and the results were compared with both the experimental phase equilibrium compositions and the MWDs of each phase. The predicted results approximated the experimental results in the hexane-rich phase, and the predicted and experimental results qualitatively agreed in the PE-rich phase.

The present work was focused on the ethylene + hexane + polydisperse PE system, and the LL phase boundary was measured and correlated to adjust the interaction parameter of the ethylene – PE pair. The LL phase equilibria were then simulated to clarify the effect of the addition of ethylene into the hexane + polydisperse PE system. Moreover, the effect of the polydispersity of PE on both the LL phase boundary and phase equilibria were also investigated.

2. Experimental

The polydisperse PE used in the present work was the same as that used in the previous work [13], and was supplied by Sigma–Aldrich Co. The number average molecular weight (\bar{M}_n), weight average molecular weight (\bar{M}_w), and polydispersity index (\bar{M}_w/\bar{M}_n) were 7.07 kg/mol, 30.0 kg/mol, and 4.24, respectively, and were determined using the results from the gel permeation chromatography in previous work. The MWD of the polydisperse PE used is described in Fig. 1. Hexane was also purchased from Sigma–Aldrich Co., and its purity was >99 mol%. Ethylene with purity >99.9 vol% was purchased from Sumitomo Seika Co. All chemicals were used without further purification. The specifications of the chemicals used in the present work are summarized in Table 1.

The LL phase boundary of the ethylene + hexane + polydisperse PE was measured via a synthetic method using a variable-volume optical cell. A detailed explanation of the apparatus and procedure for the LL phase boundary measurement is provided in our previous papers [9–11], and, therefore, these are only briefly described here. A particulate PE with a certain weight was introduced directly into the cell, and the inside of the cell was evacuated. Ethylene was then introduced into the cell using a small sample cylinder via a freeze-thaw method. Finally, hexane was added into

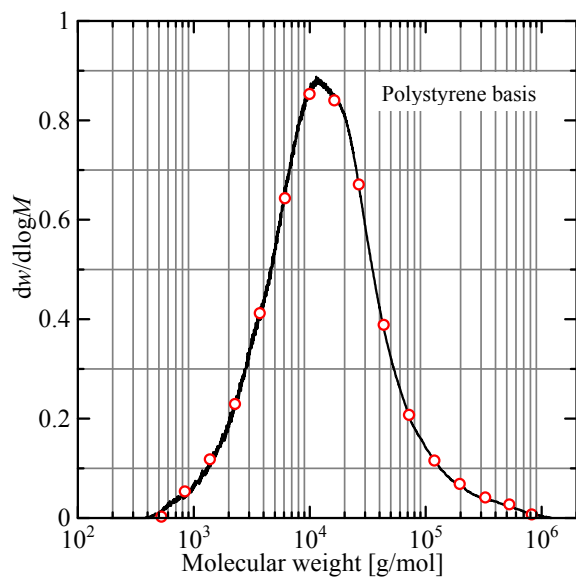


Fig. 1. MWD of polydisperse PE used. Solid line shows the MWD obtained via GPC analysis. Open circles show the representative 16 pseudo-components used for the calculations via S-L EOS.

Table 1
Specifications of chemicals used in the present work.

Chemical name	Purity	Source	CAS No.
ethylene	>99.9 vol%	Sumitomo Seika Co.	74-85-1
hexane	>99 mol%	Sigma–Aldrich Co.	110-54-3
polyethylene	–	Sigma–Aldrich Co.	9002-88-4

the cell using an HPLC pump. The uncertainty of the amounts of ethylene and the hexane introduced was estimated to be within ± 2 and ± 10 mg, respectively. As the total amounts of components introduced were generally about 5 g, the uncertainty of the feed weight fraction of each component was estimated to be within ± 0.002 .

The LL phase boundary is generally determined by identification of the phase transition at which a transparent liquid phase changes to a cloudy phase by decreasing the pressure at a constant temperature and feed composition. However, the phase transition points were difficult to recognize at high PE weight fractions because the transition from a transparent phase to a cloudy phase proceeded in a gradual manner. In the present work, a method for identifying the boundary between transparent and cloudy phases was mainly used, and the results at a high-feed PE weight fraction were compared with the results obtained by observing the elimination of the interface of the separated LL phases by carefully increasing the pressure in a step-by-step manner.

3. Calculation model

The Sanchez–Lacombe (S-L) EOS was used to correlate the LL phase boundary and to simulate the LL phase equilibria. The S-L EOS is expressed as follows [14,15]:

$$\tilde{\rho}^2 + \tilde{P} + \tilde{T} \left[\ln(1 - \tilde{\rho}) + \left(1 - \frac{1}{r}\right) \tilde{\rho} \right] = 0 \quad (1)$$

$$\tilde{P} = \frac{P}{P^*}, \quad \tilde{\rho} = \frac{\rho}{\rho^*}, \quad \tilde{T} = \frac{T}{T^*}, \quad r = \frac{MP^*}{RT^*\rho^*} \quad (2)$$

where P^* , ρ^* and T^* are characteristic parameters of the S-L EOS, and r is the segment number—the number of lattice sites occupied by molecules. M and R are the molecular weight and universal gas constant, respectively. For m -component mixtures, the mixing rules of the characteristic parameters are given by the following equations:

$$P^* = \sum_{i=1}^m \phi_i P_i^* - \frac{1}{2} \sum_{i=1}^m \sum_{j=1}^m \phi_i \phi_j \Delta P_{ij}^* \quad (3)$$

$$\Delta P_{ij}^* = P_i^* + P_j^* - 2(1 - k_{ij}) \sqrt{P_i^* P_j^*} \quad (4)$$

$$T^* = P^* \sum_{i=1}^m \left(\frac{\phi_i T_i^*}{P_i^*} \right) \quad (5)$$

$$\frac{1}{r} = \sum_{i=1}^m \left(\frac{\phi_i}{r_i^0} \right) \quad (6)$$

Download English Version:

<https://daneshyari.com/en/article/201267>

Download Persian Version:

<https://daneshyari.com/article/201267>

[Daneshyari.com](https://daneshyari.com)