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Phase Behavior and Phase Equilibria for The Polydisperse Polyethylene + Ethylene + Hexane System at High Pressures and Temperature: Experiments and Correlations

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ABSTRACT

This study aims to provide experimental phase equilibrium and phase behavior data for polydisperse PE + ethylene + hexane system. Polydisperse PE (M_w 30.0 kg/mol, PDI 4.2) was used with feed PE weight fraction, $w_{F,PE}$, of 0.02 to 0.20. The experiments based on a synthetic method were conducted at 473.2 K using an apparatus consisted of an equilibrium cell equipped with sampling tubes for solvent-rich and polymer-rich phases. The LL phase separation pressure increased by about 1 MPa for 1 wt% increase in ethylene concentration. The weight fraction of PE in solvent-rich phase, $w_{S,PE}$, decreased as the $w_{F,PE}$ and pressure decreased. Similarly, the weight fraction of PE in polymer-rich phase, $w_{P,PE}$, also decreased as the $w_{F,PE}$ decreased. The solvent-rich phase contained lower molecular weight fractions of PE, while the polymer-rich phase contained higher molecular weight fractions. These results were correlated and predicted with the Sanchez-Lacombe (S-L) EoS. Finally, the effects of pressure and $w_{F,PE}$ on solvent recovery ratio were investigated with the S-L EoS. The results provided in this study could be used to obtain the higher hexane recovery by controlling the LL separation pressure.

1. Introduction

Polymers have become the most important synthetic materials since the beginning of the 20th century along with steel and cement. Total estimation of polymers manufactured to date is 8300 Mt, with polyethylene (PE) as the majority with 36% of the total product [1]. Solution polymerization is one of the conventional industrial processes for PE due to a high-quality product with the flexibility to add co-monomer; however, it requires enormous energy to remove the solvent. This problem could be solved by the introduction of a liquid-liquid (LL) separator before solvent removal in the production process [2,3]. Therefore, phase equilibrium and phase behavior data for PE solution systems are necessary for process design.

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Previous studies have presented the LL phase behavior for monodisperse PE systems investigating the effects of PE molecular weight, temperature and ethylene addition on the phase boundary [4-13]. In our previous work, the LL phase equilibria and phase behavior for polydisperse PE + hexane system were studied [14].

Unfortunately, to the best of our knowledge experimental phase equilibrium data for polydisperse PE + hexane + ethylene system is not available. Therefore, this study focuses on providing experimental phase equilibrium and phase behavior data for polydisperse PE + ethylene + hexane system. The effect of ethylene addition on LL separation pressure and the phase equilibria will be discussed. The S-L EoS will be used to correlate LL phase behavior and to predict LL phase equilibrium data. Furthermore, the effects of pressure and $w_{F,PE}$ on solvent recovery ratio will be investigated with the S-L EoS. The results provided in this study could be used to obtain the higher hexane recovery by controlling the LL separation pressure.

2. Methodology

2.1 Materials

The polydisperse PE used for the phase equilibrium and phase behavior measurement was purchased from Sigma-Aldrich and was the same as that used in the previous work (Haruki *et al.*, 2016b). The weight average molecular weight, \bar{M}_w , number average molecular weight, \bar{M}_n , and polydispersity index, \bar{M}_w/\bar{M}_n , were 30.0 kg/mol, 7.07 kg/mol and 4.24, respectively, which were determined using a gel permeation chromatography (GPC) system (HLC-8321 GPC/HT, Tosoh Corp.) with the method described in McClellan *et al.*, [14]. The molecular weight distribution (MWD) of the polydisperse PE used is shown in Figure 1. Hexane with purity >99 mol% and ethylene with purity >99.9 vol% were purchased from Sigma-Aldrich and Sumitomo Seika Co., respectively. All chemicals were used without further purification.

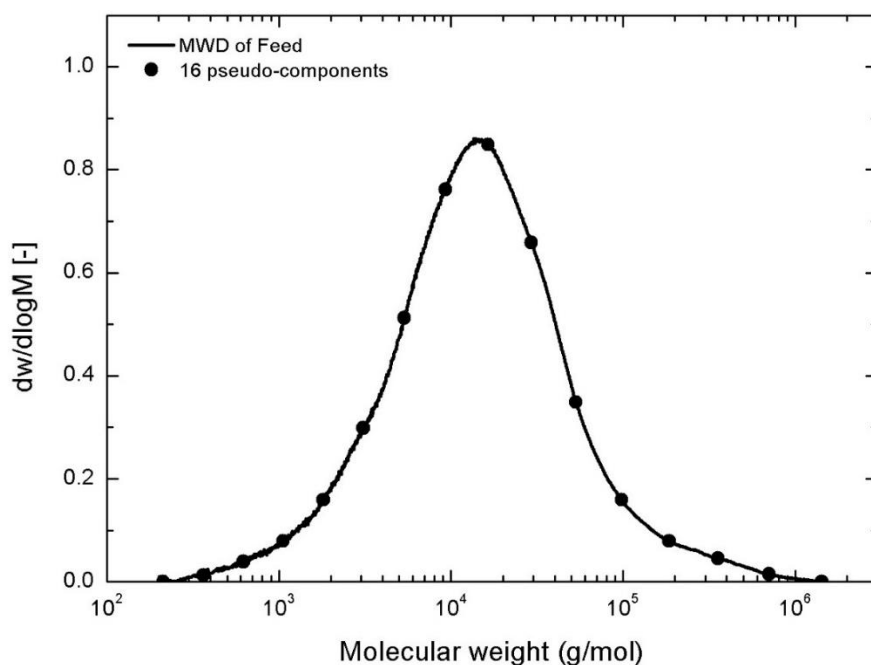


Fig. 1. The molecular weight distribution of polydisperse PE used

2.2 Experimental Apparatus and Procedure for Measurement of LL Phase Behavior

The LL phase behavior data were measured using an apparatus mainly consisted of a variable-volume optical cell, a hand pump and a charge-coupled device (CCD) camera connected to a personal computer. The details of the experimental apparatus and the experimental procedure for the cloud point measurement were explained in McClellan *et al.*, [14] and Nagy *et al.*, [15]. However, in this work, a significant modification of the experimental procedure was made to improve the accuracy of phase separation pressure measurement. First, a known amount of polydisperse PE, hexane, and ethylene were introduced separately into the variable-volume optical cell and the mixture was pressurized and heated up to an experimental temperature. The mixture was then stirred vigorously at a high pressure for 1 hour. The stirrer was then turned off, and the mixture was maintained at the temperature and pressure for a maximum of 8 hours observing the position of LL interface. This procedure was repeated by changing pressure at an interval of 0.1 MPa. The LL phase separation pressure was determined as the highest pressure at which the LL interface could be observed. This modification of experimental procedure is because the polydisperse PE systems were cloudy even in single liquid phase region and the conventional cloud point measurement could not be used to determine true phase separation pressures. The LL phase behavior was investigated at a temperature of 473.2 K, feed PE compositions (ethylene-free) ranging from 2-20 wt% and ethylene compositions of 5 and 10 wt%.

2.3 Experimental Apparatus and Procedure for Measurement of LL Phase Equilibria

The LL phase equilibrium measurement was carried out using an apparatus shown in Figure 2. The apparatus is similar to that used in the phase behavior measurements, but is equipped with two sampling tubes outside the optical cell for solvent-rich phase and polymer-rich phase. The detailed description of the apparatus and the experimental procedure was given in McClellan *et al.*, [14]. In this work, a new sampling tube shown in Figure 3 was designed to improve the sampling process. In our previous sampling tube, the free piston in the sampling tube was moved by the pressure difference between the sample and back-pressure nitrogen gas. However, the movement of the free piston was sometimes not smooth, resulting in a large pressure change of the mixture in the optical cell during sampling procedure. The new sampling tube has a screw rod as a stopper of the free piston. This modification could minimize the pressure change during the sampling process.

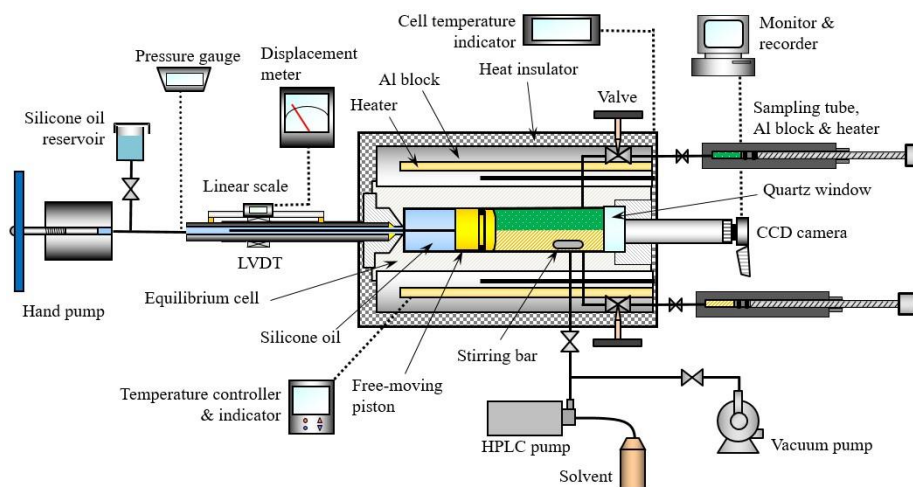


Fig. 2. Experimental apparatus for the phase equilibrium measurement

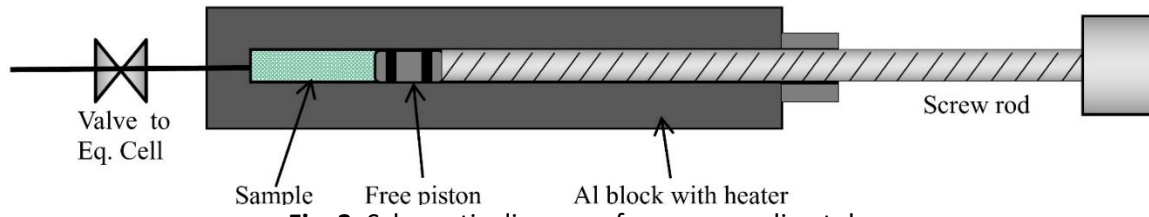


Fig. 3. Schematic diagram of a new sampling tube

The experimental procedure of the phase equilibrium measurement is as follows. First, a known amount of polydisperse PE, hexane, and ethylene were introduced into the equilibrium cell. The mixture was stirred at an experimental temperature and at a high pressure to form a homogeneous liquid phase. Then the mixture was depressurized gradually under a constant temperature to a designated pressure lower than the phase separation pressure. After reaching the designated pressure, the stirring was stopped and the mixture was left to settle for a maximum of 8 hours until the position of LL interface was unchanged. Parts of the samples in both liquid phases were then introduced to the sampling tubes slowly using a hand pump and the screw rod of the sampling tubes. The composition of each phase was determined via a gravimetric method after separating three components from the sampling tube. Furthermore, the MWD of PE in each phase was analyzed using GPC. The experiments were conducted at a temperature of 473.2 K and pressures of 10.0, 11.0 and 12.0 MPa with feed PE compositions (ethylene-free) ranging from 7.5-20.0 wt% and feed ethylene composition of 10.0 wt%.

3. Calculations

In this work, the S-L EoS was used to correlate the LL phase separation pressures and to predict the LL phase equilibria. The S-L EoS is described as follows [16,17].

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

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

where P^* , T^* and ρ^* are the characteristic parameters of the S-L EoS while r is the segment number. M and R are the molecular weight and universal gas constant, respectively. The mixing rules of the characteristic parameters for mixtures are described as follow:

$$P^* = \sum_i \phi_i P_i^* - (1/2) \sum_i \sum_j \phi_i \phi_j \Delta P_{ij}^* \quad (3)$$

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

$$T^* = P^* \sum_j \phi_j^0 T_j^* / P_j^* \quad (5)$$

$$1/r = \sum_j \phi_j^0 / r_j^0 \quad (6)$$

$$\phi_i^0 = (\phi_i P_i^* / T_i^*) / \sum_j (\phi_j P_j^* / T_j^*) \quad (7)$$

$$\phi_i = (w_i / \rho_i^*) / \sum_j (w_j / \rho_j^*) \quad (8)$$

where k_{ij} represents the binary interaction parameter and w_i denotes the weight fraction of the i -th component.

To express the polydispersity, the PE used was divided into 16 pseudo-components as shown in Figure 1. The detailed procedure for LL phase behavior correlation and phase equilibria prediction using the S-L EoS were extensively explained in the McClellan *et al.*, [14] and Sanchez and Lacombe [18]. The S-L EoS characteristic parameters used in this study are listed in Table 1, while the binary interaction parameter k_{ij} is listed in Table 2. The k_{ij} for the hexane-ethylene pair have been determined by correlating the experimental vapor-liquid equilibrium data for hexane + ethylene system [10]. The k_{ij} for the PE-ethylene pair have been determined by correlating the LL phase boundary curve for the PE + hexane + ethylene system measured in Sanchez and Lacombe [18]. Also, from our previous work, the k_{ij} for the PE-hexane pair was determined to be dependent on the molecular weight of the PE fractions, while the k_{ij} between PE fractions with different molecular weights were set to zero [14].

Table 1
 Characteristic parameters of the S-L EoS

Component	P^* [MPa]	T^* [K]	ρ^* [kg/m ³]
PE	359 ^a	521 ^a	1300 ^b
Hexane	298 ^c	476 ^c	775 ^c
Ethylene	335 ^d	285 ^d	648 ^d

^aSato *et al.*, [19], ^bMcClellan *et al.*, [14], ^cNagy *et al.*, [16],
^dTrumpi *et al.*, [20]

Table 2
 The value of binary interaction parameter k_{ij} for S-L EoS

Binary pair	k_{ij}	Reference
PE-hexane	0.029 - 0.006 x log(M[kg/mol])	McClellan <i>et al.</i> , [14]
PE-ethylene	-0.1706	Sanchez and Lacombe [18]
hexane-ethylene	0.0515	Haruki <i>et al.</i> , [10]

4. Results and Discussion

4.1 The LL Phase Behavior

The experimental LL phase separation pressures for polydisperse PE + hexane + ethylene system was measured at PE compositions (ethylene-free) ranging from 2-20 wt%, at ethylene compositions of 5 and 10 wt% and at 473.2 K. Figure 4 shows the experimental results along with reference data for polydisperse PE + hexane binary system from McClellan *et al.*, [14] as comparison. The ethylene addition to the polydisperse PE + hexane system increased the phase separation pressure at almost the same magnitude over all $w_{p,PE}$ range. This effect is known as the anti-solvent effect of a compound with low boiling point [18]. The LL separation pressure increased by about 1 MPa with 1 wt% increase in ethylene concentration.

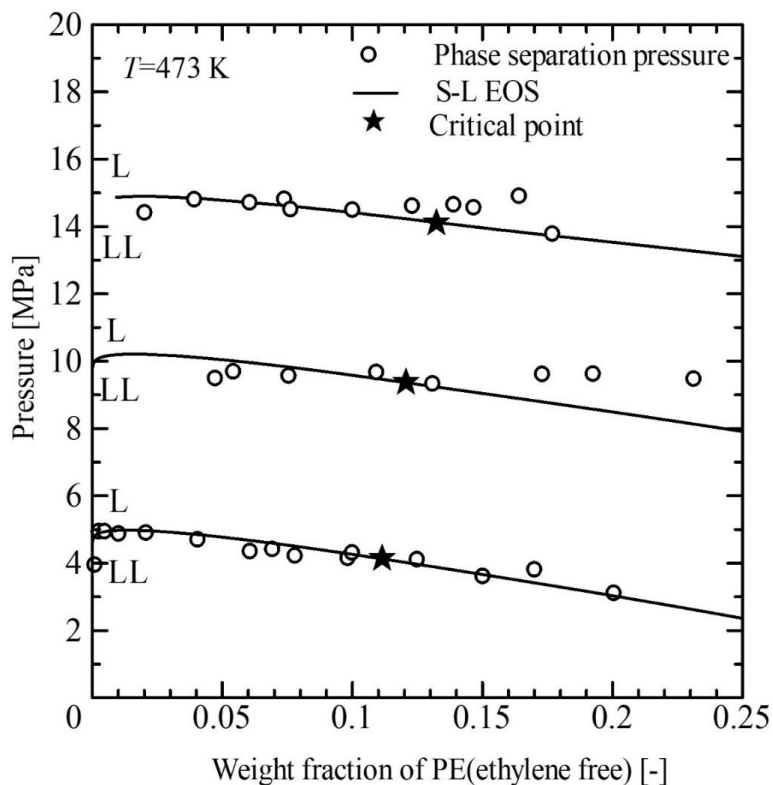


Fig. 4. Phase behavior for polydisperse PE + hexane + ethylene system

Comparing with phase separation pressures for the binary system, those for the ternary system were independent of PE composition, although the phase separation pressure should decrease slightly with increasing PE composition in high PE composition range. The reason for this is unknown, but in this range the mixtures in the optical cell were cloudy and an entanglement of PE chains might prevent reaching a thermodynamic phase equilibrium.

The S-L EoS was used to correlate the experimental phase behavior data of polydisperse PE + hexane + ethylene system. As can be seen in Figure 4, the correlation results are generally in a good agreement with the experimental data at $w_{F,PE}$ lower than about 15 wt% for ethylene compositions of 5 and 10 wt%. However, at $w_{F,PE}$ higher than 15 wt% the experimental data for the ternary system started to deviate slightly from the correlation line.

The critical weight fraction of PE, $w_{C,PE}$, was also calculated to investigate the effect of ethylene addition, because $w_{C,PE}$ is an important parameter to understand the separation phenomena; namely, bubble point type or dew point type. As is seen in Figure 4, the calculated $w_{C,PE}$ (ethylene-free) slightly increased as the ethylene concentration increased. This will be because ethylene dissolves in solvent-rich phase more than in polymer-rich phase.

4.2 The LL Phase Equilibria

The LL phase equilibria were investigated at PE compositions (ethylene-free) of 7.5, 10.0, 15.0 and 20.0 wt%, ethylene composition of 10.0 wt%, pressures of 10.0, 11.0 and 12.0 MPa, and temperature of 473.2 K. The experimental phase equilibrium data and predicted results using the S-L EoS are presented in Figure 5 (top side) as well as the phase behavior data at ethylene composition of 10 wt%. In order to compare phase equilibria, the data for the polydisperse PE + hexane binary system is also presented in Figure 5 (bottom side) [14]. In the ternary system containing 10 wt% of

ethylene, the solvent-rich phase appeared at $w_{S,PE}$ less than 0.06, while the polymer-rich phase appeared at $w_{P,PE}$ higher than 0.30, in the range of experimental conditions studied. Compared to the binary system, the difference between $w_{S,PE}$ and $w_{P,PE}$ became wider. Although the values change with pressure, it will be concluded that the addition of ethylene in polydisperse PE + hexane system can remove more solvent from PE solutions.

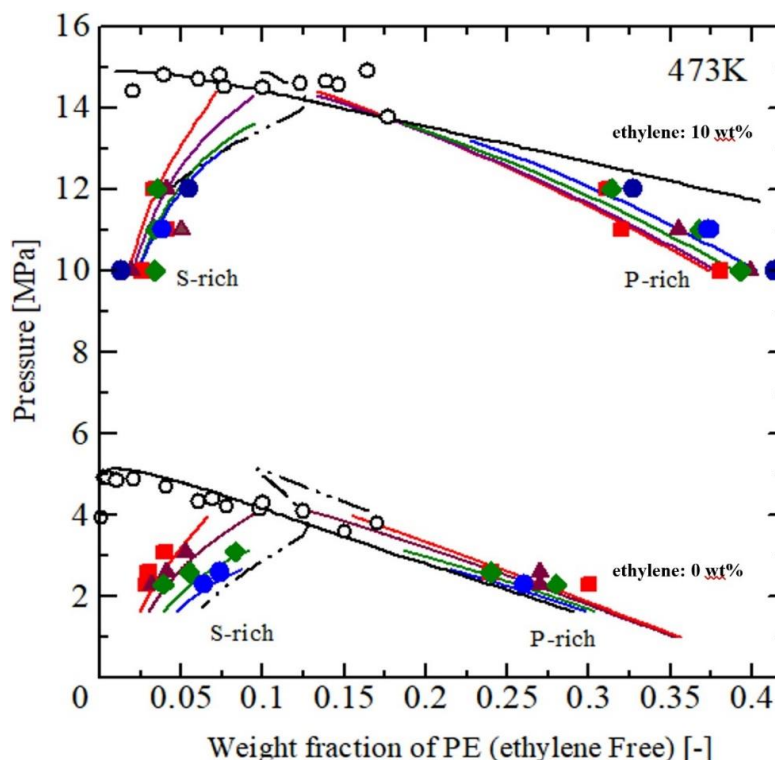


Fig. 5. Experimental and predicted LL phase equilibria for the polydisperse PE + hexane + ethylene (ethylene 10wt%) and polydisperse PE + hexane systems at 473 K. Symbols (■, ▲, ◆, ●) denote the experimental phase equilibria at $w_{F,PE}$ 0.075, 0.10, 0.15 and 0.20, respectively. Symbol (○) denotes the experimental LL phase boundary data. The black solid and dashed lines represent the correlated LL phase boundary curve and predicted shadow curve by the S-L EoS, respectively. The red, purple, green and blue lines represent the predicted phase equilibrium curves for the $w_{F,PE}$ of 0.075, 0.10, 0.15 and 0.20, respectively

Figure 5 shows that in the ternary system, both $w_{S,PE}$ and $w_{P,PE}$ increased as $w_{F,PE}$ increased. The trend for the solvent-rich phase was the same as that in the binary system [14]. However, the trend for the polymer-rich phase is the opposite; $w_{P,PE}$ decreased as $w_{F,PE}$ increased in the binary system. The position of phase equilibrium data in the polymer-rich phase was also different for these two systems. For the binary system most data in the polymer-rich phase existed above the correlated phase boundary line, whereas they existed below the line for the ternary system. These trends were consistent with those predicted by the S-L EoS in Sanchez and Lacombe [18]. The presence of ethylene should promote these changes in phase equilibria, but it will be difficult to explain theoretically its effect without the prediction by EoS.

The prediction of phase equilibria for the ternary system was performed by the S-L EoS with k_{ij} values just the same as those used in the phase behavior correlation. In the solvent-rich phase the predicted results generally represented the experimental data. The differences between the

predicted and the experimental results might be caused by the small scattering of experimental data. As for the polymer-rich phase, the predicted results approximately reproduced the experimental results, which were more scattered compared to those in solvent-rich phase. The high viscosities of the polymer-rich phase might make it harder to collect the sample during the sampling process and to separate each component for composition analysis.

The PE samples obtained from polymer-rich and solvent-rich phases were analyzed using Gel Permeation Chromatography (GPC) and an example of the results is presented in Figure 6. The solvent-rich phase contained lower molecular weight fractions of PE, while the polymer-rich phase contained higher molecular weight fractions. This means that by introducing an LL separator, it is possible to remove low molecular weight fractions that degrade the quality of the PE product. These results were satisfactorily predicted with the S-L EoS.

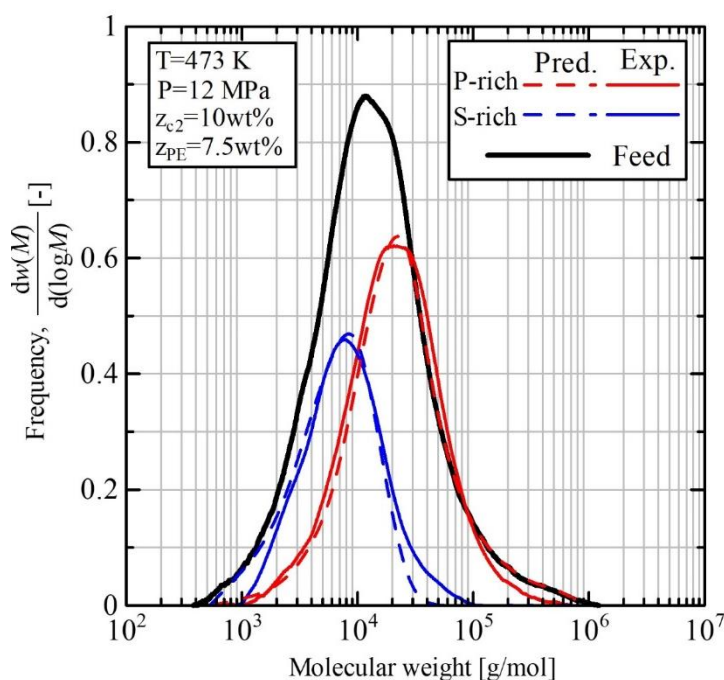


Fig. 6. Experimental and predicted MWD of PE in each phase

The experimental and predicted weight average molecular weight (\bar{M}_w) of PE in polymer-rich and solvent-rich phases are presented in Figure 7. While \bar{M}_w values in polymer-rich phase were similar to that of the feed PE, \bar{M}_w values in solvent-rich phase were much lower than it. The predicted \bar{M}_w was consistent with experimental data, although the experimental data showed some scattering.

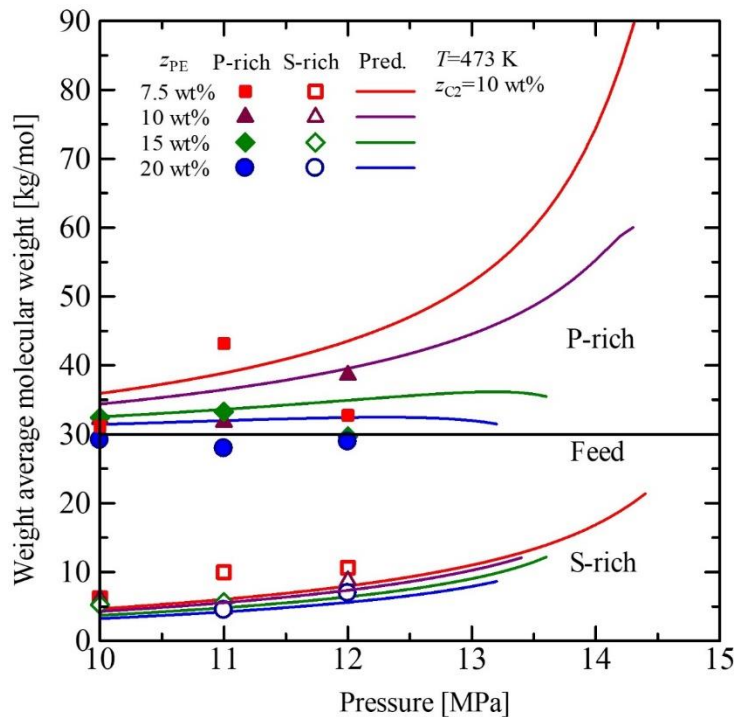


Fig. 7. Experimental and calculated weight average molecular weight (\bar{M}_w) for both phase

The effects of pressure and $w_{F,PE}$ on solvent recovery ratio were investigated using the S-L EoS. The hexane recovery ratio (H_R) was defined as the ratio of hexane amount in the solvent-rich phase to that in initial feed. This value is essential in the design of PE production process. From the calculated results presented in Figure 8, it could be seen that high H_R values of more than 0.8 were obtained at $w_{F,PE}$ lower than the $w_{C,PE}$ (around 13%). On the other hand, above the $w_{C,PE}$ the H_R increased as the pressure decreased. This profile could be used to obtain maximum hexane recovery by careful selection of the $w_{F,PE}$ and LL separation pressure.

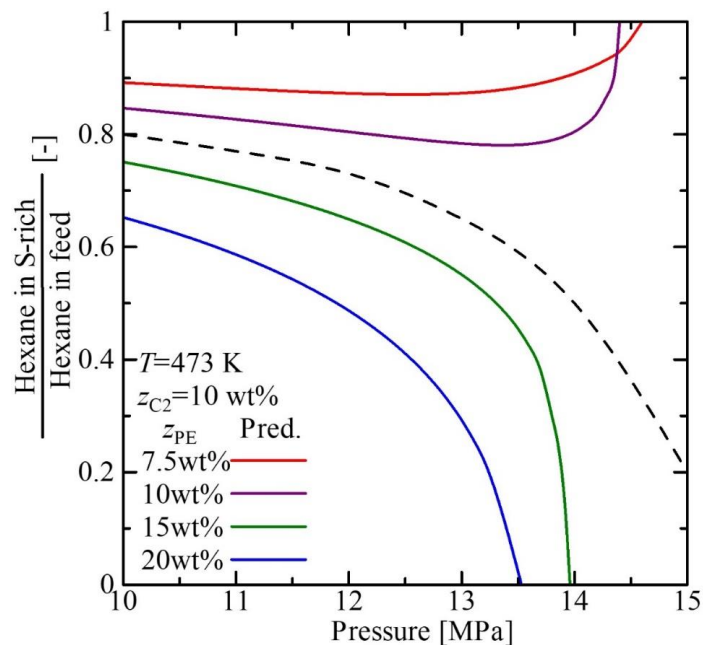


Fig. 8. Calculated hexane recovery ratio

5. Conclusions

In this work, the LL phase behavior and phase equilibria for the polydisperse PE + hexane + ethylene system were measured at 473.2 K. For the phase behavior, the LL separation pressure increased by about 1 MPa for 1 wt% increase in ethylene concentration, and the dependence of PE composition on the phase separation pressure became small as ethylene composition increased. For the phase equilibria, the difference in PE compositions in both liquid phases became wider as pressure decreased. The PE compositions in both the phases increased with increasing feed PE compositions, which was different tendency from that in polydisperse PE + hexane binary system. From GPC analysis it was found that LL phase separation can widely remove lower molecular weight fractions of PE as well as polymerization solvent. The S-L EoS was able to correlate the phase behavior data and predict the LL phase equilibria as well as molecular weight distributions of PE in both phases, satisfactorily. Finally, hexane recovery ratio was investigated from the predicted results using the S-L EoS. The investigation will give useful information for the optimum design of PE production process.

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