

Phase Behavior of Ternary Mixture of Poly(ethylene-co-octene) - Ethylene - 1-Octene

Jin-Eun Sohn, Sung-Yoon Chung,
Sang-Hoon Han and Sang-Ho Lee[†]

Department of Chemical Engineering, Dong-A University,
Hadan2-dong, Saha-gu, Busan 604-714, Republic of Korea

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Poly(ethylene-co-octene) - Ethylene - 1-Octene 3성분계 혼합물의 상거동

손진언 · 정성윤 · 한상훈 · 이상호[†]
동아대학교 화학공학과

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ABSTRACT: Cloud-point data to 160 °C and 1,000 bar are presented with poly(ethylene-co-15.3 mole% octene) copolymers (PEO₁₅) in pure 1-octene and mixtures of ethylene - 1-octene. The cloud-point curves for PEO₁₅ - ethylene - 1-octene mixture dramatically increase in pressure to as high as 1,000 bar with an increasing ethylene concentration. At ethylene concentrations less than 18 wt%, the ternary mixture has bubble- and cloud-point curves. As the ethylene concentration of the ternary mixture increases, the bubble-point curve and the single-phase region reduce. The reduction in the single phase region with increasing ethylene concentrations is the result of reduced dispersion interactions between PEO₁₅ and the mixed solvent. The single-phase region decreases with increasing temperatures when ethylene concentrations are lower than 36 wt%, whereas the single-phase region increases with temperatures at ethylene concentrations greater than 50 wt%. At ethylene concentrations greater than 50 wt% the effect of the polar interactions of the mixed solvent, which is unfavorable to dissolve PEO, is greater than the effect of the density of the mixed solvent. Therefore, the cloud-point pressures increase with a decreasing temperature. However, at ethylene concentrations less than 50 wt%, the cloud-point pressures decrease with temperature, because the effect of the polar interactions is less than the density effect.

요약: Poly(ethylene-co-15.3 mole% octene) (PEO₁₅) - 1-옥텐 2성분계 혼합물과 PEO₁₅와 (에틸렌 + 1-옥텐) 혼합용매로 이루어진 3성분계 혼합물의 상거동을 160°C와 1,000 bar의 영역까지 측정하였다. PEO₁₅ - 에틸렌 - 1-옥텐 혼합물에서 에틸렌의 함량이 증가함에 따라 cloud-point 곡선이 측정되는 압력이 급격하게 높아졌다. 에틸렌 함량이 18 wt% 보다 낮을 경우, PEO₁₅ - 에틸렌 - 1-옥텐 혼합물에서 bubble-point 곡선과 cloud-point 곡선이 모두 관측되었다. 에틸렌 함량이 증가함에 따라 PEO₁₅ - 에틸렌 - 1-옥텐 혼합물에서 bubble-point 곡선이 관측되는 온도 범위는 좁아졌으며, PEO₁₅ - 에틸렌 - 1-옥텐 혼합물이 단일상으로 존재하는 온도-압력 영역이

[†]대표저자(e-mail : Sangho@dau.ac.kr)

현저히 감소하였다. 에틸렌 함량에 따라 단일상 영역이 감소하는 것은 PEO₁₅와 (에틸렌 + 1-옥텐) 혼합용매 사이에 작용하는 분산인력이 줄어들기 때문이다. 에틸렌을 36 wt% 보다 적게 함유한 PEO₁₅ - 에틸렌 - 1-옥텐 혼합물의 단일상 영역은 온도가 높아짐에 따라 감소하였다. 이와는 대조적으로 에틸렌을 50 wt% 보다 많이 함유한 PEO₁₅ - 에틸렌 - 1-옥텐 혼합물의 단일상 영역은 온도가 높아짐에 따라 증가하였다. PEO₁₅ 용해도를 낮추는 혼합용매 사이의 극성인력과 PEO₁₅ 용해도를 높이는 혼합용매의 밀도는 온도가 낮아짐에 따라 증가한다. 에틸렌 함량이 50 wt% 보다 많을 경우, 혼합용매들의 극성인력 효과가 밀도 효과보다 커서 온도가 낮아짐에 따라 cloud-point 압력은 증가하였다. 에틸렌 함량이 50 wt% 보다 적을 경우, 혼합용매들의 극성인력 효과가 밀도 효과보다 작아서 온도가 낮아짐에 따라 cloud-point 압력은 감소하였다.

Keywords : poly(ethylene-co-octene), phase behavior, cloud-point, ethylene, 1-Octene

I. Introduction

Poly(ethylene-co-octene) (PEO) has an octene comonomer in the backbone architecture, which donates elastomeric characteristics to the copolymer. PEO is an ethylene-based copolymer. Thus, its compatibility with thermoplastic olefins, such as polyethylene and polypropylene, is expected. PEO can be used as a compounding resin for polyolefin to improve impact property and resistance to low temperature brittleness.

Copolymer has a wide variety of monomer-comonomer composition. The properties of ethylene copolymer extensively vary with type and amount of comonomer incorporated into the backbone of the copolymers. During copolymerization, small change of comonomer concentration in the feed can cause a great change of comonomer composition in the copolymer. Because of the wide variation in copolymer properties, the phase behavior of copolymer-solutions can be rather unpredictable. Therefore, it is important to know the location of the phase boundaries for copolymer solutions in order to avoid potential fouling problems and to control the quality of copolymer. An understanding of the phase behavior of copolymer solutions is also needed to efficiently separate product copolymers from unreacted monomers and solvent.

A large number of studies have been accomplished to determine the phase behavior of the binary mixture including ethylene-based copoly-

mers.¹⁻¹¹ Several studies were performed to investigate the phase behavior of ternary copolymer mixtures. For instance, Cowie and McEwen,¹² Wolf and Blaum,^{13,14} Ratzsch and coworkers¹⁵⁻¹⁷ observed the cosolvent effect of vinyl acetate on the phase behavior of poly(ethylene-co-vinyl acetate) - ethylene mixtures. Lee et al.^{18,19} showed that adding a polar dimethyl ether and ethanol to non-polar butane greatly changes the solubility of poly(ethylene-co-acrylic acid) in the mixed solvent of dimethyl ether - butane and ethanol - butane. Meilchen et al.⁸ reported that the addition of small amounts of ethanol or acetone to poly(ethylene-co-methyl acrylate) - propane mixtures shifts the cloud-point curve to lower pressures and temperatures. Limited numbers of studies were performed on studying the phase behavior of PEO solution. Radosz et al.^{20,21} measured the phase behavior of PEO in ethylene and propane. They correlated the experimental data with Statistical Associating Fluid Theory equation of state. Lee et al.^{22,23} experimentally determined the phase behavior of PEO in various normal-hydrocarbons.

In this study, we demonstrate experimental investigation about the phase behavior of PEO₁₅ - ethylene - 1-octene systems. PEO₁₅ has 15.3 mol% of octene repeating unit in the backbone structure. The relatively long pending group of the octene repeating unit endows elastomeric characteristic to PEO. 1-octene and ethylene have a very small dipole moment of 0.3 debye and a small quadruple moment

of $1.5 \times 10^{-26} \text{ erg}^{0.5} \cdot \text{cm}^{2.5}$, respectively. 1-octene has a polarizability of $153.3 \times 10^{-23} \text{ cm}^3$, 3.6 times larger than that of ethylene. First, we determined the effect of the PEO₁₅ concentration on the solution behavior of PEO₁₅ - 1-octene system. Then, the phase behavior for PEO - ethylene - 1-octene ternary mixture was investigated. During the copolymerization process of PEO, ethylene, 1-octene, and PEO coexist at much higher concentrations than catalysts and by-products in the reactor and purifying equipments. We expect the phase behavior study of PEO - ethylene - 1-octene mixture provides fundamental thermodynamic information on the PEO process solution.

II. Experimental

1. Phase Behavior

Cloud-point and bubble-point curves are measured using a high-pressure, variable-volume cell, which has a 1.59 cm I.D., an O.D. of 7.0 cm, and a working volume of $\sim 28 \text{ cm}^3$. A 1.9 cm thick sapphire window is fitted in the front part of the cell to allow visual observation of the phases. The concentration of PEO in the PEO - ethylene - 1-octene mixture is around 5 wt%. Typically 350 ± 2 milligrams of PEO are loaded into the cell that is subsequently purged several times at room temperature with ethylene to remove any entrapped air. 1-octene is transferred into the cell using a syringe. Then, balanced amount of ethylene is transferred into the cell gravimetrically using a high-pressure cylinder.

The pressure of the mixture is measured with three Konics pressure transducers (model PT-3300, 0 ~ 9.8 bar, 0 ~ 98 bar, 0 ~ 343 bar, accuracy $\pm 0.3\%$) below 340 bar. In the high pressure region, a Heise gauge (Dresser Ind., model CM-128639, 0 to 2,068 bar, accurate to within ± 2.0 bar) is used to measure the pressure of the mixture. The temperature of the cell, which locates in an air bath, is measured using a platinum-resistance thermo-

meter (Thermometrics Corp., Class A) and a digital multimeter (Konics Co., Model KN-2300-5, accuracy $\pm 0.2\%$). The mixture temperature is typically maintained to within ± 0.2 °C. The mixture in the cell can be viewed on a video monitor using a camera coupled to a borescope (Olympus Corp., model R080-024-000-50) placed against the outside of the sapphire window. A fiber pipe connected to a high-density illuminator (Dolan-Jenner Industries, Inc., model 180) and to the borescope is used to transmit light into the cell. The solution in the cell is well mixed using a magnetic stir bar activated by an external magnet beneath the cell. At a fixed temperature, the mixture in the cell is compressed to a single phase. The mixture is maintained in the one-phase region at the desired temperature for at least 20 minutes so that the cell can reach thermal equilibrium. The pressure is then slowly decreased until the solution becomes cloudy. The cloud-point pressure is defined as the point at which the mixture becomes so opaque that it is no longer possible to see the stirring bar in the solution. The cell is then repressurized to a single phase and maintained for at least 10 minutes. The experimental measurements are repeated at least twice at each temperature, and are reproducible to within ± 1.0 bar for cloud-point. Experimental procedures are described in detail in references.^{11, 22, 23}

2. Materials

The PEO₁₅ was obtained from DuPont Dow Elastomers Corporation. Table 1 shows the properties of PEO₁₅ used in this study. Ethylene and 1-octene (all CP grade, 99.0% minimum purity) were obtained from Sigma-Aldrich Company. All solvents were used as received. Table 2 lists physical properties of solvents used in this study.^{24,25}

Table 1. Properties of Poly(ethylene-co-15.3 mol% octene) Used in This Study

	octene mol%	density (g/cm ³)	melting temperature (°C)	glass transition temperature (°C)	\overline{M}_n	\overline{M}_w	$\frac{\overline{M}_w}{\overline{M}_n}$
PEO ₁₅	15.3	0.864	50	- 59	64,800	135,500	2.1

Table 2. Physical Properties of Solvent Used in This Study^{24,25}

Substance	dipole moment (debye)	quadruple moment (esu - cm ²)	polarizability $\alpha \times 10^{25}$ (cm ³)	critical temperature T _c (°C)	critical pressure P _c (bar)	critical density ρ_c (g/cm ³)
Ethylene	0	1.5	42.5	9.4	50.6	0.214
1 - Octene	0.3	-	153.3	293.5	26.8	0.236

III. Results and Discussion

1. PEO₁₅ - 1-Octene Binary System

Figure 1 shows the effect of PEO₁₅ concentration on the pressure-temperature (P-T) behavior of PEO₁₅ - 1-octene mixture. 1-octene has a polarizability of $153.3 \times 10^{-25} \text{ cm}^3$ and a small dipole moment of 0.3 debye. In the region above the curves in Figure 1, the binary mixture of PEO₁₅ - 1-octene maintains a single homogenous phase. At P-T spaces lower than each curve, the homogenous liquid phase separates into PEO₁₅ rich liquid phase and 1-octene rich vapor phase. At temperatures less than 170°C, PEO₁₅ is dissolved at pressures below 5 bar in 1-octene. Figure 1 also shows that the single-phase region increases with decreasing temperature.

Using data in Figure 1, it is possible to plot pressure-concentration (P-x) isotherms of PEO₁₅ in 1-octene. For example, Figure 2 shows P-x isotherms for the PEO₁₅ - 1-octene mixture at 60, 120, and 160 °C. If pressures drop below each curve, the single liquid phase of PEO₁₅ - 1-octene mixture separates into PEO₁₅ rich liquid phase and 1-octene rich vapor phase. Figure 2 demonstrates that the single-phase region of PEO₁₅ - 1-octene mixture decreases with increasing temperature. As temperature increases, the pressure separating the homo-

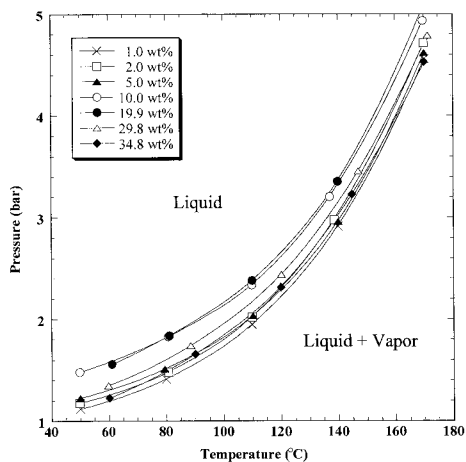


Figure 1. Effect of PEO₁₅ (15.3 mol% 1-octene) concentration on the bubble-point curves of PEO₁₅ - 1-octene mixture.

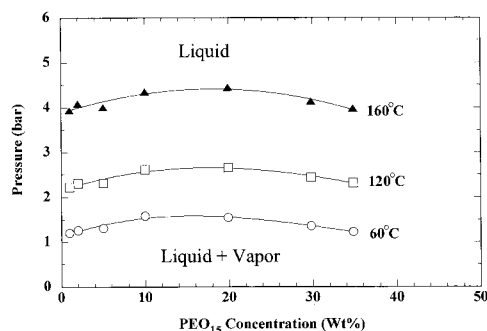


Figure 2. Pressure-composition isotherms of the PEO₁₅ - 1-octene mixture at 60, 120, and 160 °C.

geneous mixture of PEO₁₅ - 1-octene into PEO₁₅ rich liquid phase and 1-octene rich vapor phase increases. In addition, Figure 2 shows that the curves for PEO₁₅ - 1-octene mixture have maximums at the concentrations between 10 and 20 wt% PEO₁₅.

2. PEO₁₅ - 1-Octene - Ethylene Ternary System

Ethylene is a poor solvent for polymer due to its low density and polarizability. Addition of ethylene to PEO₁₅ - 1-octene mixture reduces the solubility of PEO₁₅ in the mixed solvent of 1-octene and ethylene. Figure 3 shows the phase behavior of PEO₁₅ - ethylene - 1-octene mixture that the ethylene concentration in the mixture is 15 wt%. Adding 15 wt% ethylene to PEO₁₅ - 1-octene mixture increases the pressures dissolving PEO₁₅ in the mixed solvent from 4.5 to 95 bar at 160 °C, which is about 20 times higher than the pressure in pure 1-octene. From 40 to 160 °C, the ternary mixture containing 15 wt% of ethylene has a bubble-point transition (open circles). As pressures exceed the bubble-point curve, the heterogeneous ternary mixture that has one liquid and one vapor phase merges into one single liquid phase. However, at temperatures higher than 140 °C the ternary mixture has two types of transition: bubble-point (solid line) and cloud-point curve (dashed line). The cloud-point curve intersects the bubble-point curve at 140 °C. The ternary mixture does not merge into one single liquid phase. Instead, it transforms into a PEO rich liquid and a solvent rich liquid phase. If pressures continuously increase higher than the cloud-point curve, the two liquid phases merge into one single liquid phase.

Figure 4 shows the effect of ethylene concentration on the phase behavior for PEO₁₅ - ethylene - 1-octene mixture at ethylene concentrations lower than 25 wt%. As the ethylene concentration of the ternary mixture increases, the temperature at which the cloud-point curve intersects the bubble-point curve decreases. For example, adding additional 3 wt% of ethylene to make 15 wt% ethylene concentration reduces the intersecting

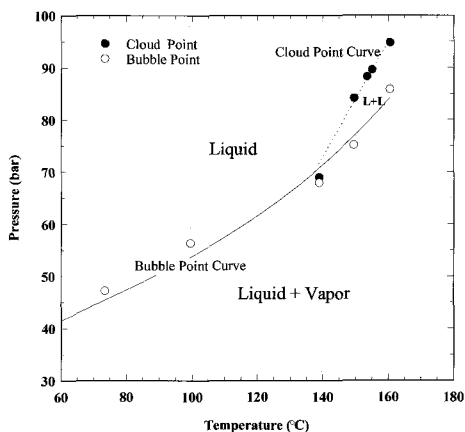


Figure 3. Cloud-point and bubble-point curve for PEO₁₅ - ethylene - 1-octene mixture at 15 wt% ethylene concentration. Open and closed circle represent bubble- and cloud-point, respectively. "L+L" means two that liquid phases coexist in the system. PEO₁₅ concentration in the solution was 5.3 wt%.

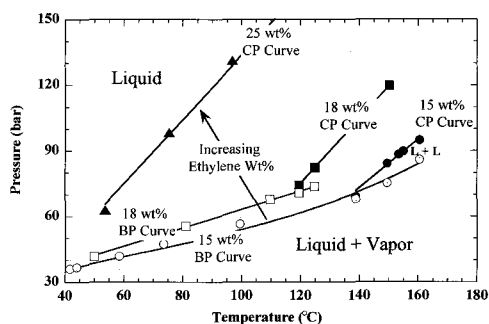


Figure 4. Effect of ethylene concentration on the phase behavior for PEO₁₅ - ethylene - 1-octene mixture at low ethylene concentrations. Open and closed symbols represent bubble- (BP) and cloud-point (CP), respectively. PEO₁₅ concentrations in the solutions containing 18 and 25 wt% ethylene were 5.7 and 4.8 wt%, respectively.

temperature from 140 to 120 °C. The intersecting temperature moves closer to the high temperature end point of the bubble-point curve as the ethylene concentration increases. Figure 4 also shows that as ethylene concentrations increase, the bubble-point curve reduces and single-phase region shrinks. When the ethylene concentration is 25 wt%, only cloud-points are observed. The pressure dissolving PEO₁₅ abruptly increases at temperatures higher than 50 °C.

The effect of high ethylene concentration on the P-T behavior for PEO₁₅ - ethylene - 1-octene mixture is shown in Figure 5. As the temperature is higher than 50 °C, the ternary mixture exhibits only cloud-point type transitions at concentrations greater than 25 wt% ethylene. The single-phase region shifts to a higher P-T space and greatly reduces with increasing ethylene concentration. For instance, adding 36 wt% ethylene into PEO₁₅ - 1-octene mixture increases the cloud-point pressures up to 270 ~ 350 bar higher than the pressure that dissolves PEO₁₅ in pure 1-octene. Adding 64 wt% ethylene raises the cloud-point pressures from 4 to 1,000 bar. The reduced solubility of PEO₁₅ results from the decrease in the dispersion interactions between PEO₁₅ and (ethylene - 1-octene) mixed solvent which is directly proportional to the polarizability of the polymer and solvent. To compensate the decreased dispersion interactions, high pressure is needed to increase the density of the mixed solvent. However, since polarizability of ethylene is too low, PEO₁₅ does not dissolve in pure ethylene even at 160 °C and 1,900 bar. Figure 5 also shows that the slope of the cloud-point curve changes from positive to negative in the P-T space as the ethylene concentration increases. The single-phase region

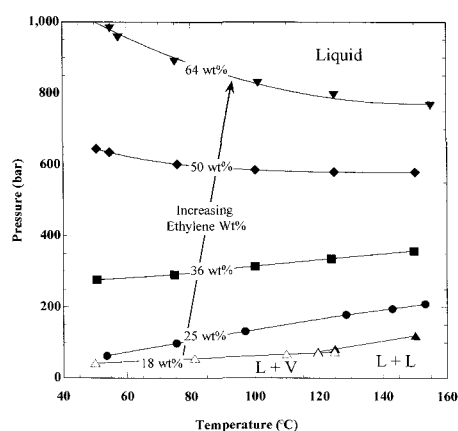


Figure 5. Cloud-point curves for PEO₁₅ - ethylene - 1-octene mixture at high ethylene concentrations. For the 18 wt% ethylene curve, open and closed symbols represent bubble- and cloud-point, respectively.

decreases with increasing temperatures when ethylene concentrations are lower than 36 wt%, whereas the single-phase region increases with temperatures at ethylene concentrations greater than 50 wt%. The negative slope of the cloud-point curves suggest that the polar interaction of ethylene begins significant at high ethylene concentrations. The polar interactions are unfavorable to dissolve non-polar PEO. Therefore, the cloud-point pressures of PEO₁₅ in the mixed solvent increase with decreasing temperatures at high ethylene concentrations.

Figure 6, which is constructed using P-T diagram in Figure 4 and 5, well demonstrates the effect of ethylene concentration and temperature on the cloud-point pressure of PEO₁₅ in the mixed solvent. At 100, 130, and 160 °C, all three cloud-point curves exhibit similar dependencies on ethylene concentration that increases with the amount of ethylene added to the ternary mixture. However, the extent of the effects of ethylene concentration on the curves varies with temperature. The slope of cloud-point curves with respect to ethylene concentration gradually increases with decreasing temperature. At 50 wt% ethylene, the cloud-point pressures are almost identical between 100 and 160 °C.

As ethylene concentration becomes greater than 50 wt%, dispersion interactions between PEO and the mixed solvent decrease due to the reduced

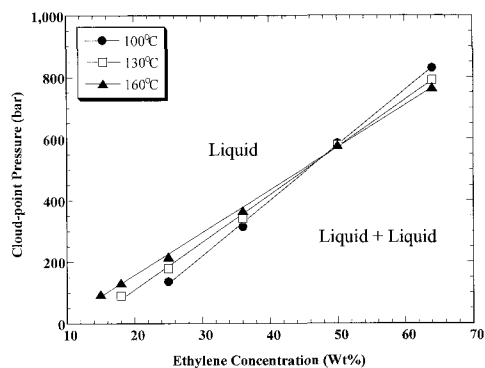


Figure 6. Cloud-point pressure for PEO₁₅ - ethylene - 1-octene mixture as a function of ethylene concentration of the mixture at 100, 130, and 160 °C.

amount of 1-octene having large polarizability of $153.3 \times 10^{-25} \text{ cm}^3$. The reduced dispersion interactions increase the cloud-point pressure of the ternary mixture. At a fixed ethylene concentration, both the density of the mixed solvent and the polar interactions between mixed solvent increase with decreasing temperatures. The increased density of the mixed solvent is favorable to dissolve PEO whereas the strengthened polar interactions are unfavorable to dissolve PEO. At high ethylene concentrations, the effect of the unfavorable polar interactions is supposed to be greater than the favorable density effect. Higher pressures are needed to dissolve PEO with decreasing temperature at the fixed concentration of ethylene higher than 50 wt% in the ternary mixture.

As ethylene concentrations become less than 50 wt%, the density of the mixed solvent as well as the dispersion interactions between PEO and the mixed solvent increase because of increasing 1-octene amount in the mixed solvent. Since the elevated density and the dispersion interactions are favorable to dissolve the PEO, the cloud-point pressure of the ternary mixture decreases. For instance, the cloud-point pressure of the ternary mixture containing 18 wt% ethylene decreases to 85 bar at 130 °C. At the fixed concentration of ethylene less than 50 wt%, the effect of increasing solvent density with decreasing temperature overwhelms the effect of the unfavorable polar interactions between the mixed solvent which also increases with decreasing temperature. Unlike the mixtures containing ethylene more than 50 wt%, the cloud-point pressures increase as temperatures rise.

IV. Conclusions

The cloud-point pressure of PEO₁₅ - ethylene - 1-octene mixture abruptly increases with the concentration of ethylene in the ternary mixture. As ethylene concentrations in the ternary mixture increase, the bubble-point curve of the ternary mixture shortens and only the cloud-point curve is

observed at ethylene concentrations higher than 25 wt% of ethylene. At 160 °C, the addition of 15 and 64 wt% ethylene to PEO₁₅ - 1-octene mixture increases the pressures to dissolve PEO₁₅ from 4.5 to 95 and 750 bar, respectively. The cloud-point pressures are about 20 and 167 times higher than the pressure that dissolves PEO₁₅ in pure 1-octene. The increasing cloud-point pressure is result of weakened dispersion interaction between PEO₁₅ and the mixed solvent due to the decreased amount of 1-octene. Also, the reduced density of the mixed solvent decreases the solubility of PEO₁₅ and increase the pressure to dissolve PEO₁₅.

The extent of the effects of ethylene on the cloud-point curves varies with temperature. The dependency of the cloud-point curve on temperature is determined by the polar interactions and density of the mixed solvent. The polar interactions, unfavorable to dissolve PEO, increase with decreasing temperatures. The density of the mixed solvent, favorable to dissolve PEO, also increases with decreasing temperatures. At ethylene concentrations greater than 50 wt%, the cloud-point pressures increase with decreasing temperatures. This suggests that the effect of the unfavorable polar interactions is greater than the favorable density effect. However, at ethylene concentrations less than 50 wt%, the cloud-point pressures decrease with temperatures. This implies that the effect of the unfavorable polar interactions is less than the favorable density effect.

Acknowledgements

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