

Influence of Polymer Molecular Weight and Concentration on Coexistence Curve of Isobutyric Acid + Water

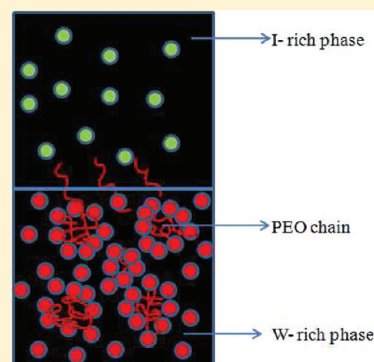
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 Supporting Information

ABSTRACT: We report the influence of variation of molecular weights (MWs = 2, 4, 6, and 9×10^5 g mol⁻¹) and concentration (C) of a long-chain polymer (polyethylene oxide, PEO) on an upper critical solution temperature (UCST) of isobutyric acid (I) + water (W) using density (ρ) measurements as a function of temperature. The ρ values in each coexisting phase of IW have been measured at three different PEO concentrations ($C = 0.395, 0.796$, and 1.605 mg/cm³) in the near critical composition of IW at temperatures below the system's upper critical point for each molecular weight (MW) of PEO. Further, to ascertain the PEO behavior in IW we have measured the polydispersity values for both coexisting liquid phases by using dynamic light scattering (DLS). The data show that the polymer was significantly affected in the critical region of IW and these various MWs and concentrations of PEO show significant modulation on the critical exponents (β), the critical temperatures (T_c), and critical composition (ϕ_c), which are depicting the shape of the coexistence curve. The values of β and T_c increase with increasing PEO MW and concentrations. Besides, the ϕ_c values slightly decrease with increasing the C values in the mixture of IW. However, the rate of decrease in ϕ_c is insignificant. Our experimental results explicitly elucidate that most of polymer chain entangles in water rich phase, thereby the polymer monomers strongly interact with neighbor solvent particles and also intra chain interaction between polymer monomers.



1. INTRODUCTION

Amphiphilic polymers have received massive attention and popularity because of their unique solution behavior and wide usage in pharmaceutical material, drug carriers, agriculture, and personal care products.^{1–4} Poly(ethylene oxide) (PEO) is an amphiphilic polymer with a molecular structure of $(-\text{CH}_2-\text{CH}_2-\text{O}-)_n$ consisting of a $\text{CH}_2-\text{O}-\text{CH}_2$ (ethylene oxide) monomer. PEO is a nonionic polymer, and its behavior in water differs from that of ionic polymers. The solubility in water and the simple structure of PEO makes it a good model system for study of the interaction mechanisms of water with polar compounds such as isobutyric acid (I).⁵ The linear long chain PEO exhibits lower critical solution temperature (LCST) behavior in many solvents including methyl, ethyl and *n*-propyl alkanol as well as acetone and both LCST and an upper critical solution temperature (UCST) behavior in water and *tert*-butyl acetate.⁶ The lower molecular weight (MW) of PEO can also form the strong hydrogen bonds with polar compound such as I by its hydrophilic nature.⁵ Besides these interpretations, it is very interesting to see the effect of PEO MW and concentration on the phase behavior of the critical binary mixture of I and water (W).

The behavior of long-chain polymer when immersed in coexisting liquid phases has remained a cornerstone of fundamental polymer science, engineering and often dictates the underlying mechanism by which everywhere technology such as coatings, paints, plastics recycling and inks, function.⁷ Conformation of a flexible linear polymer chain in a single component solvent can be

understood satisfactorily using the two parameter theory and the renormalization group theory.^{8–10} In a good solvent under dilute conditions, the polymer adopts a swollen coil-like conformation, whereas in a poor solvent the polymer chain collapses to a compact globule.

If a minute amount of a polymer (as an impurity) is added to a binary solvent, it may affect the coupling between composition fluctuations and the critical behavior. Theoretical approaches^{11–14} and numerical computer simulations^{15–19} show that when a long chain polymer is dissolved in a bicomponent mixture close to the critical solution temperature (T_c) there exists long-range indirect interaction between monomers of the polymer. The polymer might be instrumental in producing dramatic changes in the vicinity of critical point of binary solvents, thereby, the polymer would first collapse in the vicinity of the solvent critical point eventually re-expand when the correlation length of density fluctuations is larger than the size of the polymer. On the other hand, in the critical binary coexisting fluids polymer preferentially adsorbs one of the solvent components as may behaving force centers and change the properties of the system, including the local fluctuations of the concentration and critical exponents.^{18,19}

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A change in either temperature or composition of polymer solution contributes to the quality of solvent, which means that the polymer can undergo a phase transition. Such condensation from loose coil to a dense globule minimizes the polymer–solvent interactions in the poor solvent.^{20,21} In the scientific community there is vast literature on conformations of polymer by various experimental methods to reveal the conformation and behavior of a flexible linear polymer in the vicinity of the critical point of the binary solvent, and these results have received surprisingly much attention.^{4,5,22–27} However the influence of variation of polymer molecular weights (MWs) on the coexisting liquid phases has been investigated scarcely.

Interestingly, Grabowski and Mukhopadhyay²⁸ demonstrated that a polymer chain slightly contracts near the critical temperature and then expands dramatically at a temperature very close to the critical point. However, the long chain polymer behavior in coexisting liquid phases, the compatibility of expected experimental results are still not fully understood as function of MW of the same polymer and considerable confusion arises to the quality of good or poor solvents of coexisting liquid phases and the concentration of the polymer. The precise interpretation of these experiments still remains somewhat controversial in the terms of MWs of the polymer. Apparently, these considerations are particularly important not only from an academic, but also from industrial point of view.

In the field of phase transitions, besides conformational studies particular attention has also been paid for the critical exponents involved in the scaling laws, which describe the asymptotic behavior of any system near the critical point. The theoretical value of critical exponent (β) for any binary critical mixture which has a universality class is 0.325 ± 0.001 , which is in good agreement with the experimental value.^{29,30} It was already found that the value of β of the binary mixture can modulate by inclusion of polymer as in impurity.^{4,5,22–24} It appears that the β value of binary critical mixture with ionic salt is the same as that for pure mixture without ionic salt.^{31–36} In order to find out whether the conclusions^{4,5,22–24} are common for the polymer in the critical mixture or only specific for critical mixture^{29,30} or ionic salt in critical mixture^{31–36} and to properly assess the results of polymer behavior in bicomponent mixture, the knowledge of the polymer effect as a function of concentration and MWs profile at the proximity of the critical point of a binary mixture will be highly desirable. To achieve this goal, in this work, we demonstrate the effect of PEO concentration and MW on the critical point of IW.

The control variable in these systems is not only the temperature but also the MW and concentrations of the polymer. In the present study, we carried out density and polydispersity measurements on IW coexisting liquid system at its consolute point of the UCST with added PEO chains varying in MWs (2, 4, 6, and $9 \times 10^5 \text{ g mol}^{-1}$) and concentration range from 0.395 to 1.605 mg cm^{-3} under the atmospheric pressure. To interpret these measurements properly, however, we have to take into account the following phenomena: the polymer effect (1) on critical exponents (β), (2) on the critical temperature (T_c), and (3) on critical composition (ϕ_c).

2. EXPERIMENTAL METHODS

2.1. Materials. The polymer materials were all linear in architecture. Four different MWs of a linear chain PEO samples (PEO, MWs = 2, 4, 6, and $9 \times 10^5 \text{ g mol}^{-1}$) used in the present study were obtained from Aldrich Chemical Co. and were used without further purification. Water was obtained from a NANO

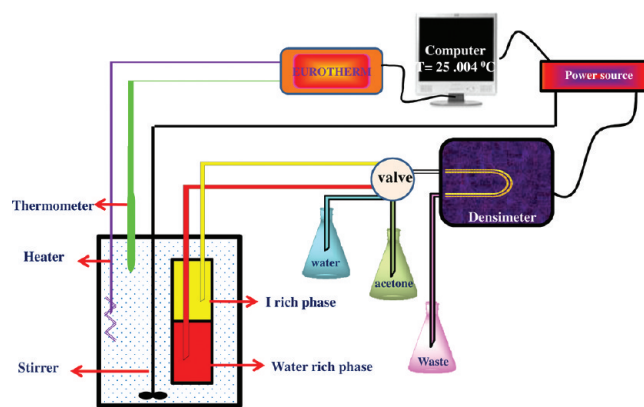


Figure 1. Schematic diagram of the experimental setup for the determination of ρ values of coexisting liquid phases, which is used in the present study.

pure-Ultra water system (Rions, New Delhi, India) that can be distilled, deionized, and degassed and a resistivity of $18.3 \Omega \cdot \text{cm}$, whereas I of 99.9% purity was purchased from Aldrich Chemical Co. and is filtered by a $0.47 \mu\text{m}$ disposal filter (Millipore, Millex-GS) before performing the experiment.

2.2. Sample Preparation. Clear solutions were prepared by taking a desirable amount of polymer through gravimetrically in analytical balance with a precision of $\pm 0.0001 \text{ g}$. Special precautions were taken in order to avoid the evaporation of I or W during the weighing process. A series of solutions ($C = 0.395, 0.796$, and 1.605 mg/cm^3) of each MW polymer in the critical binary mixture of IW were prepared by immediate capping to prevent solvent evaporation. The final solutions were all optically clear and were stirred for at least 24 h at 22°C prior to measurements. The phases form at the meniscus between two layers.

2.3. Experimental Procedure. **2.3.1. Density Measurements for Coexisting Liquid Phases of IW and PEO in IW.** The density measurements were performed as a function of temperature, using a vibrating tube densimeter (Anton Paar DMA 4500 M, Austria) with some modifications for measuring the ρ values of both phases. Figure 1 reveals schematically the experimental arrangement, which is used in the present study. The detailed procedure and apparatus used in this work have been delineated in earlier articles by Bianchi and Japas³² and Toumi and Bouanz.³⁷ A bubble-free sample was introduced into a sample cell which included a small Teflon coated magnetic bar. The cell was then sealed airtight, connected to two HPLC tubes as depicted in Figure 1, and secured in a sample holder with a water submersible magnetic stirrer. The tubing was connected to a many-way chromatographic valve, which was also connected to the vibrating tube of a densimeter. The sample holder and whole experimental setup was placed in a water bath (WB), temperature controlled to $\pm 0.002^\circ\text{C}$, made of 2 cm thick transparent plexiglass and a well stirrer was introduced into bath to circulate the water to reduce the temperature gradient. The bath temperature was monitored using a high precision thermometer which is connected to a Eurotherm temperature controller (3500 series) of a RTD probe sensor and to a personal computer (PC). The Eurotherm read the temperature and sent back the appropriate heat to the water bath through a proper controlled power supply and an electric heater. The densimeter consists of a stainless steel U-tube which is placed in a metal block, with an accuracy of $\pm 0.00005 \text{ g/cm}^3$. This instrument maintained the desired temperatures within the range of 0 – 90°C .

For each measurement, a water stationary flow was used as reference, guaranteeing also the cleanliness of the system by acetone.

Initially, the stirrer was turned on for at least 30 min to thoroughly mix the two coexisting phases inside the sample cell. After that the stirrer was turned off and the sample was left undisturbed for at least 30 min, in order for the sample to completely phase separate under gravity. Between changing the temperature and beginning the collection of the data, a period of typically 1 h elapsed. In the temperature regime studied, physicochemical measurements have shown that such a time scale is satisfactory for equilibrium, even for the measurements very near to the critical temperature.³⁸ Furthermore, no shift of the critical temperatures was observed during the measurements by checking the critical temperatures before and after density measurements. Thus, this way we ensured that both coexisting phases are in equilibrium, while we measured the densities. Samples were taken from the equilibrium vessel by the action of gravity; that is, the flow was slow and controlled. During this sample transferring from either the upper or lower phase to the densimeter, proper precautions were taken to keep the remaining phase in an undisturbed state. Prior to use, the instrument was carefully calibrated properly with nanopure water and with air as standards. By switching the chromatographic valve, alternatively upper or lower phases were introduced into the densimeter. Precautions were taken during sample injection into the U-tube to avoid air bubbles.

2.3.2. Polydispersity Measurements for PEO in IW By Using Dynamic Light Scattering (DLS). To obtain PEO behavior in IW, we measured the polydispersity values by using dynamic light scattering (DLS) experiments. These measurements were made on a 256 channel digital correlator (PhotoCor Instruments, U.S.A.) that was operated in the multitau mode (logarithmically space channels). The time scale spanned 8 decades, that is, from 0.5 μ s to 10 s. This instrument used a 35 mW linearly polarized He:Ne laser and polarized component of scattered intensity was measured. The probe length scale is defined by the inverse of the modulus of the scattering wave vector (q)

$$q = \left(\frac{4\pi n}{\lambda} \right) \sin\left(\frac{\theta}{2}\right) \quad (1)$$

where n is the medium refractive index, λ is the excited wavelength (632.8 nm), and θ is the scattering angle. In all of the experiments, the difference between the measured and calculated baseline was not allowed to go beyond $\pm 0.1\%$, and the signal modulation was maintained above 85%. Samples were prepared the day prior to the measurements. The prepared samples were placed in the temperature controlled water bath under gravity as explained in the density measurements. Thereafter, the temperature of the water bath was reduced in steps until the critical point occurred. After forming the two phases, we transferred the some of the amount from upper phase to the DLS sample cell and remaining part of the upper phase is contacting with the lower phase to maintain the thermodynamic equilibrium. During the sample transferring time, we have taken special precautions to avoid the error in polydispersity measurements. Then the airtight sample cell was placed in the thermostatted sample chamber of DLS. The Brownian motion of particles was detected by DLS and correlated to the polydispersity. The same procedure has been employed to obtain the polydispersity to the lower phase as described in the upper phase. The polydispersity values were obtained from normalized variance of the size distribution function by using the CONTIN regression instrumental software.

All PEO samples had a concentration of 0.395 mg/cm³. We noticed that there is not much variation in polydispersity of PEO for the remaining two concentrations of PEO.

2.4. Coexisting Curve of PEO in IW. The IW solvent mixture is particularly attractive, since both components (I and W) are stable over a period of a month and free from chemical decomposition. As a result, a sealed sample is likely to retain its phase separation temperature for a fairly long period of time. This system is weakly opalescent and it makes it easy to identify the phase separation temperature by visual observation. All mixtures were prepared from known masses of the pure components. Note that the binary mixture IW has an UCST of about 27 °C, so we kept the samples in a temperature-regulated bath at 30 °C overnight for them to reach equilibrium while in one single homogeneous phase.

The temperature was then decreased slowly (by a step of 0.001 °C) until a phase boundary was observed in the middle of the vial, indicating that the sample was near critical. With the sample in the sample cell, a meniscus could be seen to form in the center of the sample cell. The position of the meniscus in the center at 1 m °C below T_c indicated that the volumes of the coexisting liquid phases were equal to the naked eye indicate a feature of criticality. Equilibrium was assumed to be reached when a sharp meniscus between two phases was observed. The detailed procedure to determine the coexisting liquid phases is shown schematically in Figure 2. The precision in the determination of critical composition is ± 0.002 . The critical composition can essentially be determined independently of the T_c . With a sample of pure IW mixture, we prepared a critical sample from 2.5018 g of water and 1.5505 g of I had an UCST, T_c , of 26.924 ± 0.002 °C using the equal volume criterion. The composition of this sample was 0.3826 mass fraction (x_c) of I which is in good agreement with the literature values (Venkatesu⁵ observed $T_c = 26.921 \pm 0.002$ °C and $x_c = 0.3940$; Shresth et al.³⁹ reported $T_c = 26.250$ °C and $x_c = 0.390$; Greer⁴⁰ reported $T_c = 26.445$ °C and $x_c = 0.3793$; Xia and Maher⁴¹ reported $T_c = 26.40$; Berg and Moldover⁴² reported $x_c = 0.3940$; Seki et al.⁴³ reported $T_c = 27.05$ °C; Beysens and Bourgou⁴⁴ reported $T_c = 26.793$ °C and $x_c = 0.3889$; Morrison and Knobler⁴⁵ reported $T_c = 26.963$ °C and $x_c = 0.3830$; Bouanz and Beysens⁴⁶ reported $T_c = 26.948$ °C and $x_c = 0.390$; Bouanz⁴⁷ $T_c = 27.140$ °C and $x_c = 0.3890$).

The critical parameters and critical region of the mixed solvent system alters with the addition of a third component as an impurity to a binary liquid mixture at a critical point.^{48–50} Brochard–de Gennes theory⁵¹ makes an interesting prediction for a polymer in a mixture of two good solvents, where the affinities of the macromolecule for the two solvent components differ substantially. The prediction is that the polymer will adopt collapsed configurations as the T_c of the solvent mixture is approached, even though it would be swollen in either of the pure component solvents at the same temperature. The effect of PEO in IW has not been studied extensively; however, a few investigations^{5,39,52,53} have shown the PEO behavior in IW mixtures to understand the anomalous behavior in the vicinity of the critical point. Recently, we investigated that the phase-transition region of coexisting phases of IW alters at T is close enough to T_c with the addition of PEO ($M_w = 9 \times 10^5$ g mol^{−1}) as a function of polymer concentration by the refractive index measurements.⁵ Theories of polymers in two good mixed solvents exist,¹² but they have not been subjected to extensive experimental tests of polymer in good/poor solvents and as a function of MWs of polymer. As mentioned before, PEO was

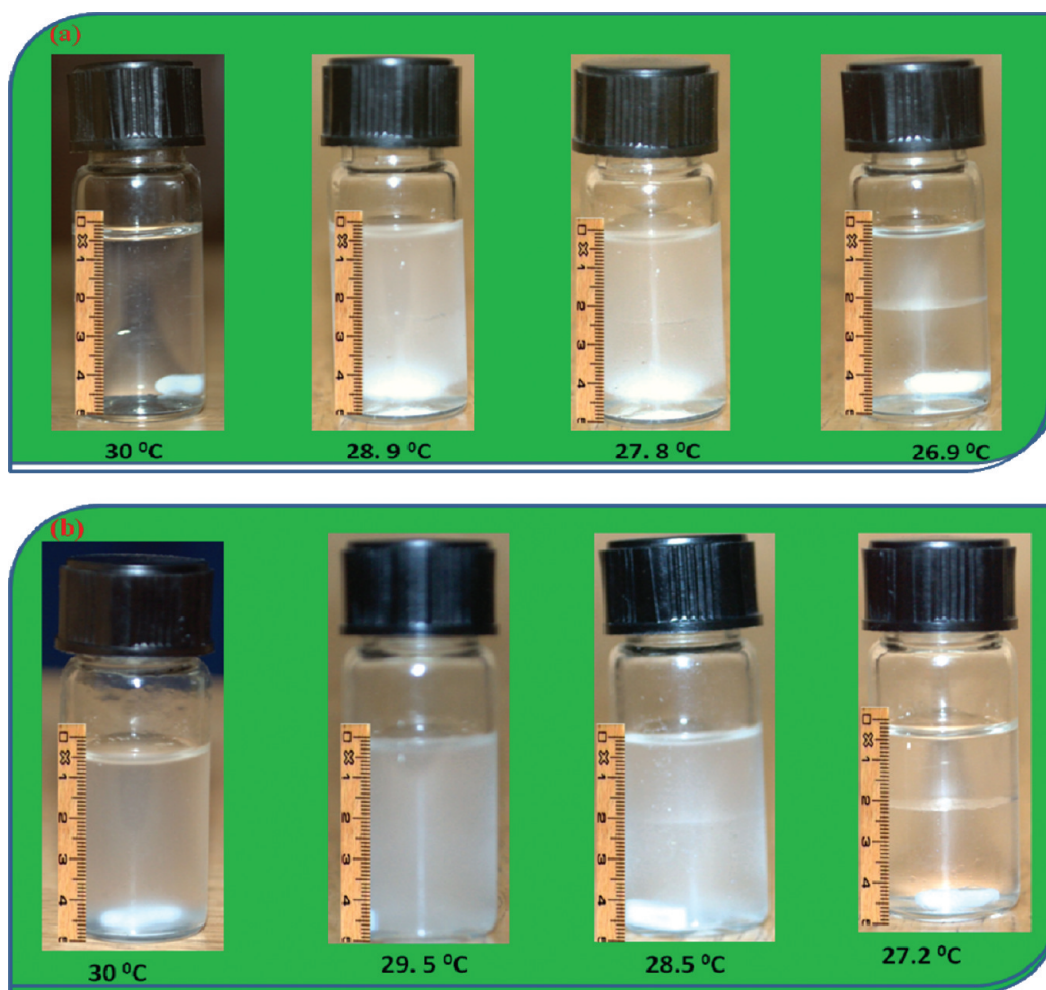


Figure 2. Determination of the critical composition of IW system (a) without and (b) with PEO of MW = $2 \times 10^5 \text{ g mol}^{-1}$ and concentration of 1.605 mg/cm^3 .

dissolved in the mixture of IW and a series of PEO concentrations ($C = 0.395, 0.796$, and 1.605 mg/cm^3) with various MWs ($2, 4, 6$, and $9 \times 10^5 \text{ g mol}^{-1}$) of every concentration were prepared separately. Each sample solution was held overnight in a water bath while stirring at a fixed temperature. After 24 h the temperature was decreased in step by step manner until the meniscus appeared in middle of the vial, as described for the method of the pure IW mixture.

3. RESULTS AND DISCUSSION

Measured ρ values are presented as a function of the temperature (T) upon approaching the critical temperature (T_c) for PEO varying MWs ($0, 2, 4, 6$, and $9 \times 10^5 \text{ g mol}^{-1}$) in coexisting liquid phases in Figure 3 and in Table S1 at three different PEO concentrations. Our results show that PEO explicitly affected in the critical region of IW in all cases. We have found that the apparent critical density (ρ_c) is $0.99365 \text{ g cm}^{-3}$ at $26.924 \text{ }^\circ\text{C}$ for pure IW system by fitting the diameter of the coexistence curve, which is in good agreement with the literature values (Jacobs and Greer⁵⁴ reported $\rho_c = 0.99300 \text{ g cm}^{-3}$; Greer⁴⁰ reported $\rho_c = 0.99300 \text{ g cm}^{-3}$; Toumi and Bouanz⁴⁸ reported $\rho_c = 0.99357 \text{ g cm}^{-3}$ at $26.945 \text{ }^\circ\text{C}$ (from graph of ref 48.). However, Jacobs and Greer^{40,54} reported apparent critical density of IW is $0.99300 \text{ g.cm}^{-3}$, which their sample was away from the critical

point (reported T_c was $25.988 \text{ }^\circ\text{C}$) which is not consistent with our T_c value.

Figure 3 depicts that the coexistence curves obviously enhance with increasing MW of PEO in IW mixture at all three investigated PEO concentrations, since a minute amount of PEO impurity only marginally affects the critical region of IW. This variation induces a modification of the phase transition region affected with the addition of PEO to IW mixture, and presumably, PEO preferentially adsorbs the water molecules. As seen from Figure 3 the ρ values of W-rich phases significantly increase with increasing MW of PEO, which is contributing to more absorption of water molecules by the polymer chain whereas those values are very slightly increased in the I-rich phase which leads to the I molecules having less affinity toward the polymer chain. The variation in absorbing water and I molecules by the PEO chain is mainly due to water ions, being stronger electron acceptors than the methylene protons of PEO, can capture the oxygen atom of PEO, thereby water strongly forms hydrogen bonds with nonbonding oxygen ($-\text{O}-$) orbitals in PEO.⁵⁵ This hydrogen-bonding requirement is easily satisfied by water without significant perturbation of the structure of the water.⁵⁶ PEO absorbs more water molecules than I molecules and this may vary with the size of PEO. Since the oxygen–oxygen distance of 2.88 \AA ⁵⁷ of PEO is close to the oxygen–oxygen distance of 2.85 \AA of pure water, the PEO chain fits into a hydrogen-bonded network

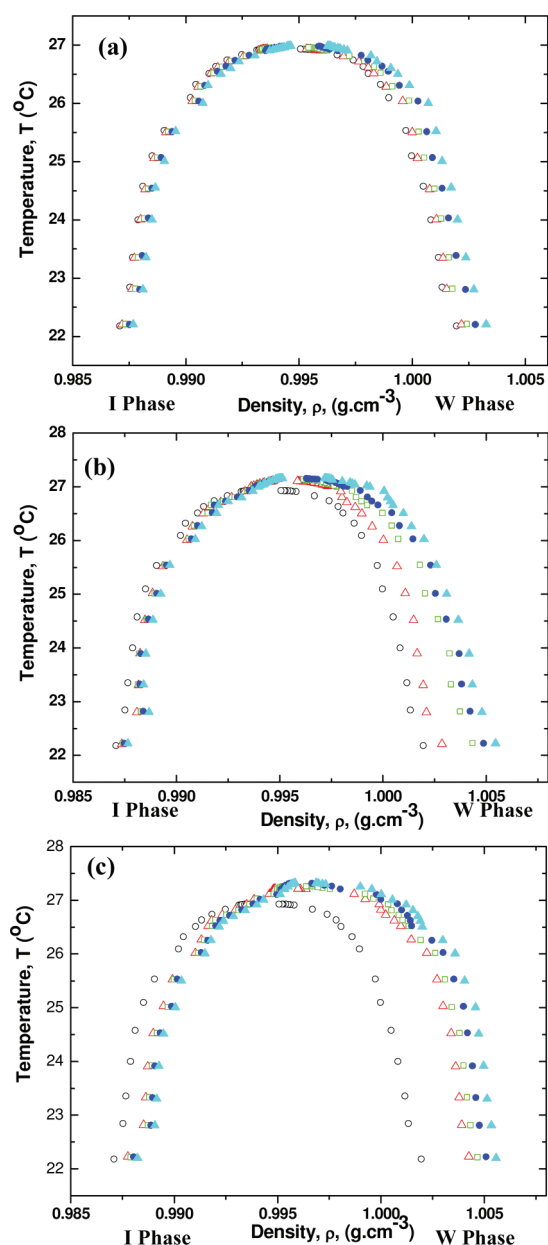
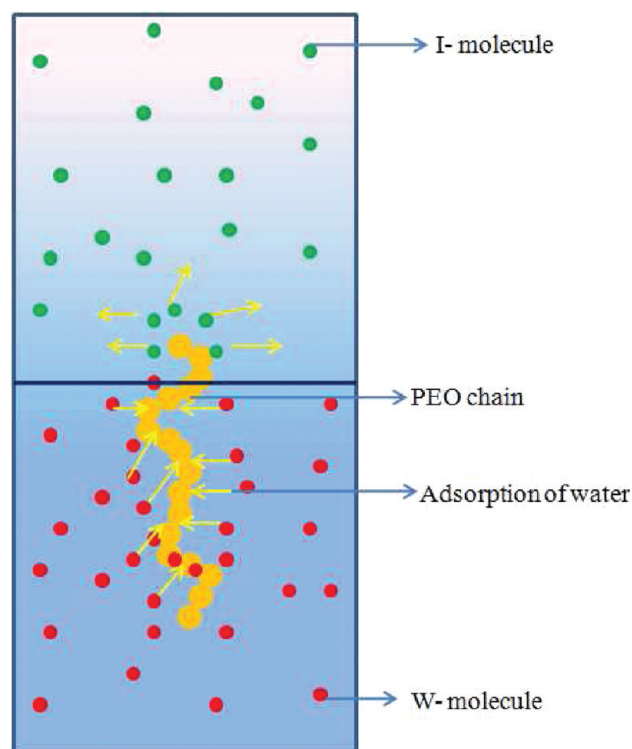


Figure 3. Coexistence curves from the temperature dependence of density measurements for IW (mass fraction, x_c of I = 0.3826) with various MWs [0 (\circ), 2×10^5 (red triangle), 4×10^5 (green square), 6×10^5 (blue circle), and 9×10^5 (blue triangle) g mol^{-1}] and different concentrations [(a) 0.395, (b) 0.796, and (c) 1.605 mg/cm^3] of PEO as a function temperature.

of water. Kjellander and Florin⁵⁷ proposed a model in which the hydrophobic CH_2CH_2 groups of PEO are shielded from contacting water molecules with cage-like structure of hydrated. Two to three water molecules per monomer form the first layer. Water spirals are formed in such a way that more water molecules accumulate on the cavities surrounding the oxygen atoms of the PEOs. A lack of significant perturbation in the structure and the fact that the ethyl moieties in the PEO chain are largely accommodated by the water structure minimize hydrophobic interactions. These facts suggest that PEO indeed has minimal interactions with other solvents such as I. This possible mechanism has been schematically shown in Scheme 1. As a result, the densities

Scheme 1. Schematic Illustration of PEO Chain Behavior in IW Coexisting Liquid Phases^a



^a An accumulation of water on the cavities surrounding the oxygen atoms of PEO. A lack of significant perturbation of PEO leads to a slight increase in density of the I-rich phase. Whereas in the W-rich phase, ethyl moieties of the PEO chain are largely accommodated by the water structure minimize hydrophobic interactions cause significant increase in density of this phase. These facts suggest that PEO indeed has minimal interactions with other solvents such as the I-rich phase.

of the water-rich phase significantly increase with increasing MW of PEO, whereas those values slightly increase in I rich phase (Figure 3).

To obtain a more detailed picture of the role of the PEO chain on the phase separated IW system, the experimental density values of the pure IW mixture and with three varying PEO concentrations of lower ($2 \times 10^5 \text{ g mol}^{-1}$) and higher ($9 \times 10^5 \text{ g mol}^{-1}$) MWs of PEO are summarized in Figure 4 as a function of the temperature (T) upon approaching the critical temperature (T_c). Careful examination of Figure 4 reveals that ρ values slightly increase in I and significantly increase in W rich phases with increasing the concentration of PEO at lower MW of PEO. Similar results are clearly visible in Figure 4b for higher MW of PEO. Apparently, at $C = 0.395 \text{ mg/cm}^3$ and low MW of PEO, the polymer solvent interactions are not enough to cause collapse of chains, since we observed a slightly variation of ρ values in the W-rich phase. However, at higher $C = 1.605 \text{ mg/cm}^3$, we observed a rapid increase in ρ values at the W rich phase. The results in Figures 3 and 4 explicitly elucidate that the water molecules interact more strongly with polymer monomers than I molecules (Scheme 1). These interactions increase with increasing both MWs and concentration of PEO in the IW system. These observations indicate the MWs and concentrations of PEO independently affecting on the critical region of IW. One interpretation of the inverse solubility–temperature relationship

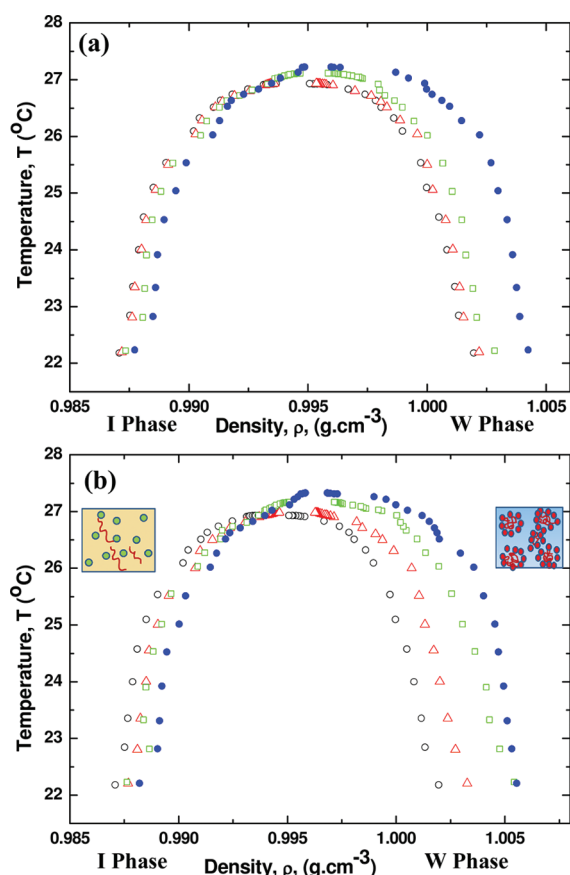


Figure 4. Coexistence curves from density measurements for IW (mass fraction, x_c of I = 0.3826) with various concentrations [0 (○), 0.395 (red triangle), 0.796 (green square), and 1.605 (blue circle) mg/cm^3] and MWs [(a) 2×10^5 and (b) 9×10^5 g mol^{-1}] of PEO.

of the PEO chain in water solution, that is, a hydrophilic–hydrophobic balance, exists in which water molecules are oriented relative to the polyether chain via hydrogen bonding. Obviously, it could be estimated that three water molecules were closely associated with each oxyethylene unit in the chain, wrapping around the polyether chain in a hydrogen-bonded and helical fashion.⁵⁸ This preferential adsorption effect might change intra- and interchain correlations. The large dielectric constant ($\epsilon = 78.36$ at 25°C)⁵⁹ of water serves to lower the dissociation energy of the ions allowing them to separate more easily compared to the lower dielectric constant of I ($\epsilon = 40$).⁵⁹ At the same time, the hydrogen bonding of PEO/water is strong and competes with ion complexation. Graphical representations in Figures 3 and 4 show that the coexistence curves obviously enhance with increasing PEO MW as well as concentration in IW mixture. This is because PEO is more adsorbing in water than I, which makes both coexisting phases mutually less soluble and therefore rises in UCST of IW with addition of PEO. According to Timmermans rules,⁶⁰ when the third component is equally soluble in both coexisting liquid phases that lead to increase in lower critical solution temperature (LCST) and decrease in UCST. If the third component is more soluble in one liquid component than in the other, then we expect that the mutual solubility will be decreased, thus it leads to increase in an UCST and decrease in LCST values. Our results strongly consistent with the Timmermans rules as well as with the results of Alessietal et al.²⁷ However, as will be shown later, other important critical parameters β , T_c and ϕ_c are strongly

Table 1. Observed Critical Temperature (T_c), Critical Exponent (β), and Critical Density (ρ_c), as a Function of MW (MW) at Various Concentrations (C) of Polymer in the IW (Mass Fraction, x_c of I = 0.3826) System

C (mg/cm^3)	MW ($\times 10^5$ g mol^{-1})	UCST,		
		$T_c \pm 0.002$ ($^\circ\text{C}$)	β	$\rho_c \pm 0.00005$ ($\text{g}\cdot\text{cm}^{-3}$) [*]
0	0	26.924	0.326 ± 0.007	0.99365
	2	26.936	0.328 ± 0.005	0.99460
	4	26.950	0.335 ± 0.003	0.99477
	6	26.972	0.340 ± 0.007	0.99543
	9	26.986	0.347 ± 0.008	0.99565
0.395	2	27.108	0.377 ± 0.010	0.99525
	4	27.131	0.383 ± 0.007	0.99557
	6	27.148	0.395 ± 0.004	0.99568
	9	27.161	0.407 ± 0.002	0.99618
	2	27.281	0.415 ± 0.009	0.99609
1.605	4	27.297	0.438 ± 0.002	0.99616
	6	27.309	0.449 ± 0.004	0.99623
	9	27.322	0.451 ± 0.009	0.99643

^{*} Critical ρ values obtained by fitting the diameter of the coexistence curve for all investigated samples.

affected in the presence of impurity in the polymer free system of the critical point. Table 1 lists the values of T_c , β , and ρ_c for IW samples with and without PEO at the critical temperatures for the mixtures of IW with a series of PEO MWs at different PEO concentrations (0, 0.395, 0.796, and 1.605 mg/cm^3).

3.1. Effect of MW of PEO on Critical Exponent (β) In I + W at Various Concentrations of PEO. To get better insight into the influence of PEO on the critical mixture of IW as a function of MWs and concentration of PEO, we predicted the values of β . These results have been shown in Figure 5. To interpret the experimental results, in the vicinity of the critical point, we obtained the value of β , from the density measurements of two coexisting phases with the relative distance from the T_c . For evaluating β , we used the relation $(\Delta\rho \equiv \rho_1 - \rho_2) \propto (\Delta T \equiv T_c - T)^\beta$ where ρ_1 and ρ_2 are the densities of the two coexisting phases. The experimental data were analyzed with a properly weighted linear least-squares fit⁶¹ to the simple scaling relationship $\Delta\rho = B\Delta T^\beta$, where B is critical amplitude. The error in $\Delta\rho$ was taken as ± 0.00005 g cm^{-3} , and the error in ΔT was ± 0.0028 $^\circ\text{C}$. Fits were performed using the commercially available program ORIGIN 8.1. The obtained value of $\beta = 0.326 \pm 0.007$ and the critical amplitude $B = 0.017 \pm 0.004$ for a free polymer of the IW binary mixture is in agreement with the three-dimensional Ising value $\beta = 0.325$ as well as with the results found in various studies by several researchers. Our results are strongly consistent with the results of Stein and Allen,⁶² who analyzed the coexisting curve data and found a value of $\beta = 0.345 \pm 0.021$. Greer⁴⁰ observed a value of $\beta = 0.328 \pm 0.004$ from the density measurements for phase separated system of IW. Furthermore, Beysens et al.⁶³ observed a value of $\beta = 0.328$, which was obtained by the reanalyzed experimental density of ref 40. Andrew et al.⁶⁴ determined a value of $\beta = 0.326 \pm 0.003$, Bouanz and Beysens⁴⁶ reported 0.325 ± 0.015 , and Venkatesu⁵ reported 0.326 ± 0.007 by refractive index measurements of IW. Subsequently, we consider all data points for obtaining the critical values of β for the remaining systems of the PEO in IW.

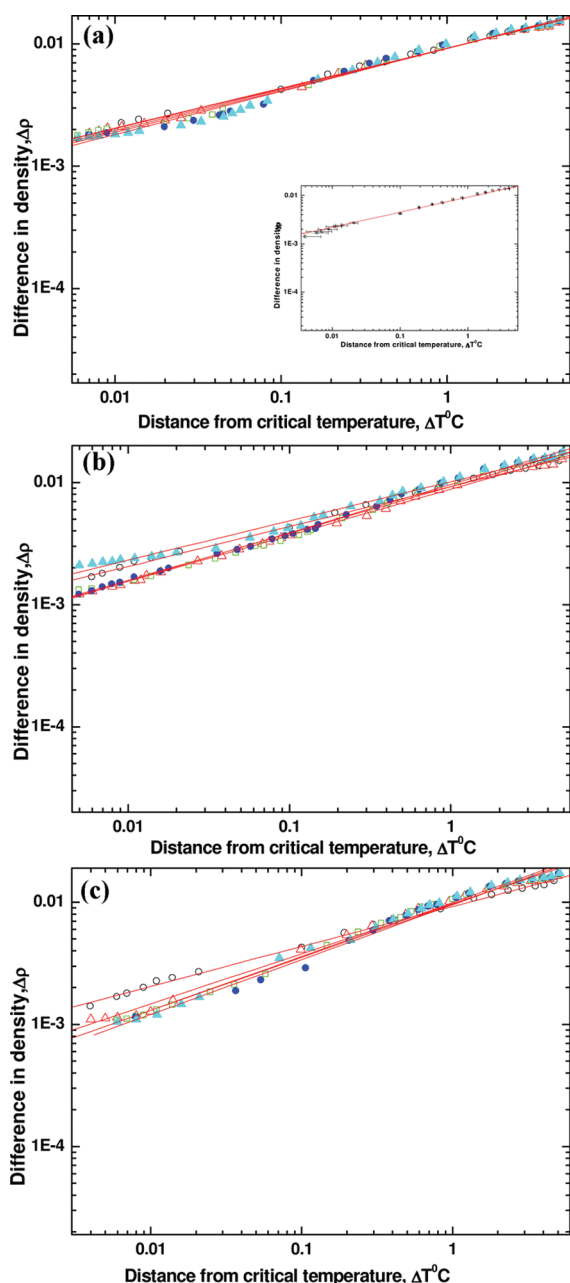


Figure 5. Logarithmic representation of density difference $\Delta\rho$ between the two coexisting phases with respect to the distance from the critical temperature ΔT for IW (mass fraction, x_c of $I = 0.3826$) and various PEO in IW [MWs = 0 (\circ), 2×10^5 (red triangle), 4×10^5 (green square), 6×10^5 (blue circle), and 9×10^5 (blue triangle) g/mol] at (a) 0.395, (b) 0.796, and (c) 1.605 mg/cm^3 concentrations of PEO. The inset shows $\Delta\rho$ as a function of ΔT for pure IW. The solid line represents the results of fit. For the sake of simplicity and clarity, we did not show the fits and error bars for PEO in the IW system.

Figure 6 illustrates the effect of the change of MWs ($2, 4, 6$, and 9×10^5 g/mol) on β with various concentrations (0.395, 0.796, and 1.605 mg/cm^3) of polymer. The value of β is obtained by extracting the slope from the plot of $\log(\Delta\rho)$ vs $\log(\Delta T)$. As seen from Figure 6, β values increase with increasing the MWs and as well as concentrations of PEO. The results from Figure 6a clearly show that β values slightly increase with increasing the MWs of PEO at 0.395 mg/cm^3 concentration. Further these values

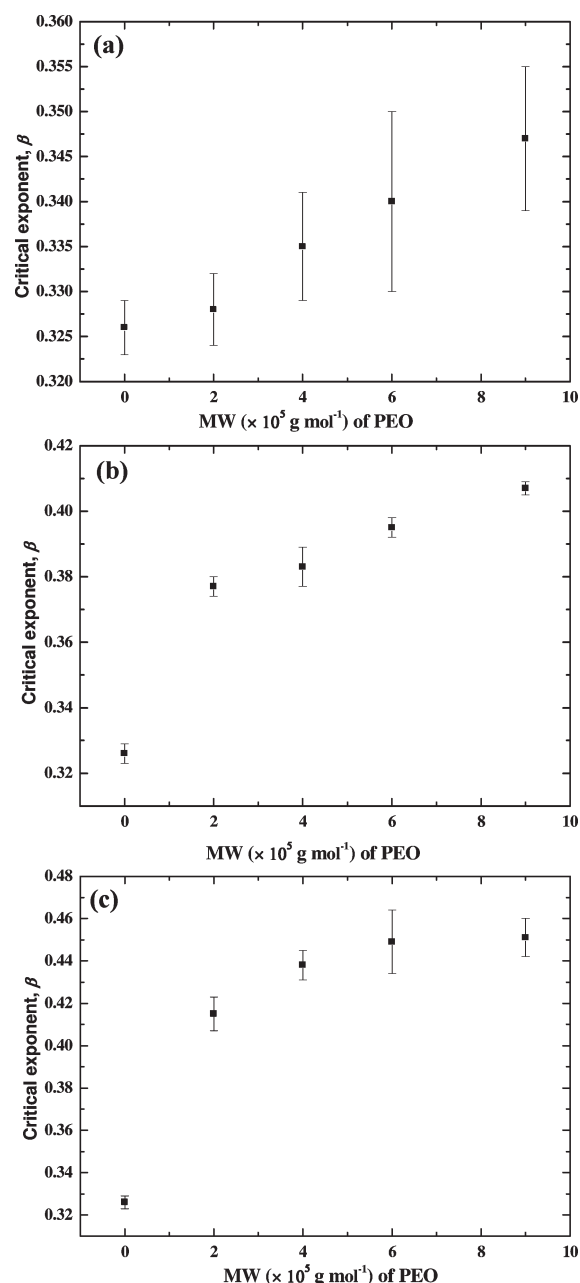


Figure 6. Polymer effect on critical exponent β as a function of PEO MWs [$0, 2 \times 10^5, 4 \times 10^5, 6 \times 10^5$, and 9×10^5 g/mol] in IW (mass fraction, x_c of $I = 0.3826$) at various concentrations [(a) 0.395, (b) 0.796, and (c) 1.605 mg/cm^3] of PEO, and the errors indicate the standard deviation.

increase moderately with increasing MWs of PEO at 0.796 mg/cm^3 (Figure 6b). Eventually, we observed rapid enhancement in β values at higher concentration (1.605 mg/cm^3) of PEO (Figure 6c). These results explicitly elucidate that, after the addition of a small amount of PEO into IW, β values abruptly increased as shown in Figure 6. It is worth noting that the observed β values of PEO (as an impurity) in IW are fully renormalized critical exponents, which is consistent with the theory of Broseta and Leibler.⁶⁵ This may indicate that the addition of polymer, however, produces changes in intrachain interactions between the segments of PEO and an indirect attraction between the polymer chain and the

solvent molecules. The interaction with the monomers of PEO is more favorable for the W-rich phase than the I-rich phase. When PEO is added in small concentrations to IW, PEO preferably adsorbs to molecules of solvents, and thus changes occur in particle surfaces. In addition, the impurity induces an important change in the location of the critical region of the binary system. Since PEO does not have any bulky side groups or fixed charge groups, local steric and electrostatic hindrances are expected to be minimal (at 20 °C, the steric parameter $\sigma = 1.38-2$)⁶⁶ and the chain's flexibility and mobility can help to accommodate the PEO with water or I molecules and continuous structural rearrangements with water. Therefore, the hydrophilic character of PEO is supported by its known solubility in both solvents, adsorption on PEO surfaces. These results suggest the reason for the polymer collapse.

The critical exponent β varies with PEO concentrations. For instance, the values obtained for β are 0.347 ± 0.008 , 0.407 ± 0.002 , and 0.451 ± 0.009 for higher MW of PEO at three different concentrations 0.395, 0.796, and 1.605 mg/cm³, respectively (Table 1). Similar trends were observed for the remaining systems. Obviously the addition of a polymer, at different concentrations, may induce a renormalization of the critical exponents. It is clear that this exponent increases with increasing PEO concentration in IW as shown in Figure 6. This may be due to the fact that the polymer chain greatly contracts in the critical mixture, due to an indirect attraction between the polymer chain and the solvent molecules. Analogously, similar trends were observed from our previous refractive index results for PEO (MW = 9×10^5 g mol⁻¹ as an impurity) in an UCST behavior of nitroethane (NE) + 3-methylpentane (MP), since NE is a better solvent of PEO than MP. In this study, we found that the values of β are 0.456 ± 0.015 , 0.399 ± 0.014 , and 0.372 ± 0.015 for various concentrations 0.373, 0.759, and 1.509 mg/cm³, respectively.

In contrast, these results are different from the measurements²⁴ of the high MW of poly(acrylic acid) (PAA) (MW = 7.5×10^5 g mol⁻¹) into 2,6-lutidine + water (LW) that the β values were not changed when the PAA concentration changes from 0.35 to 0.70 mg/cm³ in LW. Nevertheless, as pointed out by To,²⁴ the β value for PAA into LW was found to be 0.410 ± 0.020 , which is higher than that (0.310 ± 0.010) of the pure LW sample, since LW has an inverted coexistence curve with a LCST and water is a better solvent for PAA than lutidine. Possible reasons for these differences are related to the solvent quality and to the MW of the polymer chain. Furthermore, most probably a higher MW of PEO than PAA significantly affected the value of β of IW or NE/MP and is changing with varying the PEO concentration. Subsequently, a similar appearance has been observed in the coexistence curve of polystyrene (PS II, MW = 7.19×10^5 g mol⁻¹) in polystyrene (PS I, MW = 1.72×10^4 g mol⁻¹) + methylcyclohexane (MC) by using the refractive index measurements by Dobashi et al.^{67,68} According to their results, the critical exponent of PS I + MC changes from 0.335 ± 0.001 to 0.384 ± 0.004 when PS II was added to PS I + MC. However, the entire shape of the coexistence curve for PS II in the PS I + MC system was entirely different from those for the binary system.⁶⁸ Besides these, the PEO²³ slowly increased the inherent viscosity exponent from 0.0417 to 0.0437, with an addition of PEO to tetrahydrofuran and water (THF/W). It should be noted that the authors of these reports monitored phase behavior of binary solvent by the addition of the polymer. On the basis of these findings, it seems that the polymer is affecting the critical region of the binary solvent mixture and it is entirely plausible that it is increasing the polymer

concentration in the phase separated binary system; the changing of exponent values obviously depend on the quality of the solvents. Furthermore, we noticed that the critical exponent is closely related to the behavior of the critical point and the third component such as a polymer, which modifies the critical exponents of the coexisting liquid phases.

Our experimental results clearly reveal that PEO is able to modify the β values of the IW binary critical mixture. We wish to address one interesting point that the impurities effect the β values in binary critical mixtures rather than PEO. Jacobs and co-workers also observed this by refractive index measurements of water⁶⁹ or acetone⁷⁰ used as an impurity in the critical binary mixture of methanol + cyclohexane (ME + CH) and pointed out that the impurity (0.10 vol % of water or 1.0% of acetone) enhances the critical exponent of ME + CH. Subsequently, Bouanz and Beysens³¹ have noted that the critical exponent of IW with cesium bromide (CsBr) was found to be 0.320 ± 0.015 which was almost the same (0.313 ± 0.010) as that of pure IW. Bianchi and Japas³² observed that $\beta = 0.328 \pm 0.010$ by the coexistence curve of water + 1,4-dioxane with potassium chloride (salt-saturation condition) on density measurements. Moreover, the coexisting phases of water + 3-methyl pyridine with sodium bromide (fixed composition) on the measurements of the refractive indices by Gutkowski et al.³³ determined that the value of $\beta = 0.326 \pm 0.010$ and also on the refractive indices measurements of the coexistence of tricritical point of the ternary system water + 3-methyl pyridine with sodium bromide (10–17 mass %), and by Wagner et al.³² predicted that the value of β at all concentrations was 0.325. It appears that the β value of binary critical mixture with ionic salt is the same as that for pure mixture without ionic salt. In contrast, our results together with those of refs 4, 5, 23, 24, 67, and 68 explicitly showed that the critical exponent β is different for critical mixtures with and without polymer, and this finding is true whether the binary mixture has an upper critical point or a lower critical point.

3.2. Effect of MW of PEO on Critical Temperature (T_c) in I + W at Various Concentrations of PEO. To explore the effects of MWs of PEO on coexistence curves of IW, the values of T_c were confirmed by eye through observing the equal volume of phases which phase separated coexisting phases as depicted in Figure 2, and these values are displayed in Figure 7 as a function of MWs of PEO at three different concentration of PEO. The T_c 's of various MWs of PEO at three different concentrations of 0.395, 0.796, and 1.605 mg/cm³ in IW were also included in Table 1. Figure 7 explicitly explains the change in T_c of IW due to the addition of various MWs of PEO. Looking at the data in this figure, there is an immediate increase in T_c value in IW with increasing the MWs as well as concentration of PEO. This shift in T_c in the present work is consistent with Staikos and Dondos²² and Norman et al.⁵³ In 1986, Staikos and Dondos²² explicitly elucidated an interesting phenomena that the dimension of the polymer (polystyrene (PS), MW = 7700 g mol⁻¹) chain was almost constant even near the critical point of PS in cyclohexane and methanol (CH/ME) and was 46.85 °C which was obviously higher than those for a pure binary mixture CH/ME (45.77 °C). Moreover, Dobashi and co-workers^{67,68} have observed in the coexistence curve of polystyrene (PS II, MW = 7.19×10^5 g mol⁻¹) in polystyrene (PS I, MW = 1.72×10^4 g mol⁻¹) + methylcyclohexane (MC), by using the refractive index measurements, that the critical point (23.6 °C) of polystyrene (PS I) + MC was raised the critical point of PSII in PS I + MC. Furthermore, Norman et al.⁵³ studied the critical phenomena of poly(ethylene glycol)

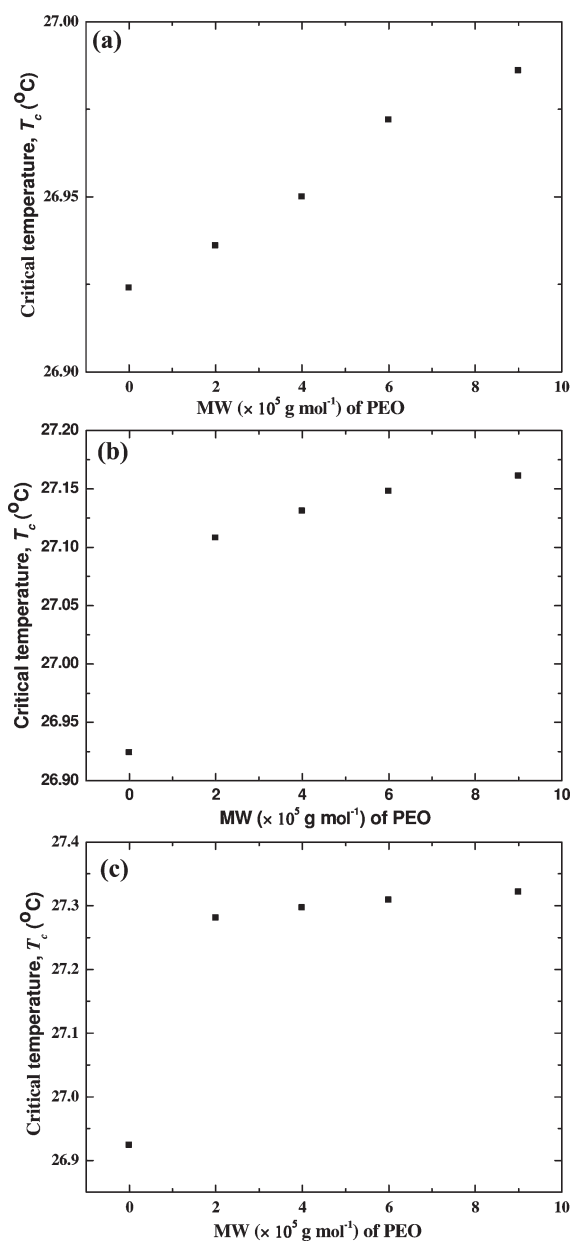


Figure 7. Polymer effect on critical temperature T_c as a function of PEO [MWs = 0, 2×10^5 , 4×10^5 , 6×10^5 , and 9×10^5 g mol⁻¹] in IW (mass fraction, x_c of I = 0.3826) at various concentrations [(a) 0.395, (b) 0.796, and (c) 1.605 mg/cm³] of PEO.

(PEG) in IW, and they found that T_c of IW increases from 26.013 to 30.528 °C with the addition of PEG to IW. In contrast to these results, Shresth et al.³⁹ observed that the critical temperature of the IW system decreased from 26.25 to 25.55 °C when 1 mg/cm³ of PEO (MW = 20 000 g mol⁻¹ as an impurity) was added to the IW critical mixture.

On the other hand, Park and Kim²³ pointed out that the addition of a very small amount of PEO into the THF/W critical mixture should produce a significant decrease in T_c of THF/W through the inherent viscosity measurements. Moreover, we have also observed⁴ that, upon addition of PEO (9×10^5 g mol⁻¹) to an UCST mixture of NE + MP, the T_c values decrease linearly with a rate of about -0.68 °C per 0.1 vol %. In other words, the T_c of a LCST of LW was decreased by approximately 0.03 and

Table 2. Observed Polydispersity Values in Each Phase of I and W (Mass Fraction, x_c of I = 0.3826) for All MWs (2×10^5 , 4×10^5 , 6×10^5 , and 9×10^5 g mol⁻¹) of PEO at the Concentration of 0.395 mg/cm³

MW (g mol ⁻¹)	polydispersity in I phase	polydispersity in W phase	difference in polydispersity
2×10^5	0.536	0.439	0.097
4×10^5	0.657	0.501	0.156
6×10^5	0.803	0.607	0.196
9×10^5	1.702	0.732	0.970

0.1 °C by adding 0.35 and 0.70 mg/cm³ of PAA, respectively. The increase in an UCST indicates that PEO molecules are more soluble in water than in I and thus makes the solvent less soluble in one another, and this observation is consistent with Timmermen rules.⁶⁰ Based on all of the above-mentioned experimental results from various researchers, clearly the polymer may either increase or decrease the critical point of the coexisting phases. These discrepancies are mainly depending on the MW of the polymer, the solvent quality, as well as critical solutions, and this conclusion is quite consistent with the theoretical results of critical polymer solutions.⁷¹

To ascertain the shift of critical points, we further performed polydispersity values near T_c using DLS technique. The results of polydispersity in both phases are tabulated in Table 2 as a function of MW of PEO. Our results explicitly elucidated that most of the polymer chain has migrated into the water rich-phase, since we observed a significant reduction of the polydispersity values in the lower phase (water). The observed polydispersity of lower MW (2×10^5 g mol⁻¹) of PEO in the water rich phase was 0.439 which is obviously a lower value than that in the acidic rich phase (0.536). Moreover, the difference in polydispersity of these two values is small (0.097). Since the migration of the molecular mass of the polymer to the respective phase affects the polydispersity of that phase, we observed a large difference in polydispersity of coexisting phases in the case of high MW of PEO, and finally this difference leads to the shift in the critical parameters. We have anticipated that the driving force for the variation in polydispersity values is related to the interactions between the polymer and solvent molecules. In addition, these results may indicate that most of the polymer long chain entangles in the water rich phase, thus the polymer chains strongly interact with solvent molecules and also intra chain interaction between polymer monomers and leads to a reduction in the polydispersity of the water phase. The present results are consistent with the existing results^{26,27,39} of the effect of the polymer chain on coexisting liquid phases through conformational changes.

3.3. Effect of MW on ϕ_c in Isobutyric Acid + Water at Various Concentrations of PEO. In the present study modulations in critical composition (ϕ_c) of IW are discussed in terms of volume fraction of I. As can be observed from the experiment, the ϕ_c values decrease with increasing the PEO MWs and concentration, since a small amount of PEO impurity in all sample solutions is most likely to be a small amount of the binary solvent.²⁴ Our results indicate that the occurrence of the PEO impurity only marginally affects ϕ_c values. The change in ϕ_c due to the presence of PEO impurity in the solution of IW could be essential in the experimental case. Presumably, when we added the PEO to IW mixture, the preferential water molecules are absorbed by PEO. Consequently, in this process some of the I molecules

migrate into the W-rich phase along with the PEO molecules (Scheme 1). Since W is a better solvent for high MW PEO than I, the W-rich phase completely wets PEO molecules, and a wetting layer was formed close to the PEO molecules. This would reduce the amount of water. Upon further compression, the adsorbed polymer starts to overlap.

As the configurative point, PEO penetrates deeply into the water rich region, and then the PEO chain entangles with water molecules. Such an entangled system may cause intrachain interactions and attraction between the polymer chain and solvent particles and this significantly causes alteration of the critical composition. Analysis of chain conformation in PEO on both phases suggests a preference for gauche rotation about C–C and a preference for the trans rotation about C–O and O–C bonds⁵⁵ in pure water. Smith et al.⁷² clearly illustrate the complex dependence of the hydrogen bonding of PEO in the molecular dynamics simulations in terms of ether oxygen in PEO/water hydrogen (O–W) and water oxygen/water hydrogen (W–W) hydrogen bonds. This interaction provides strong proof that PEO preferentially adsorbs water molecules more so than butyric acid molecules (Scheme 1). To²⁴ has also noted that a small change in critical composition by the addition of PAA into the LW. Furthermore, Norman et al.⁵³ also observed a small variation in the ϕ_c of IW with addition of PEG.

4. CONCLUSION

We have shown that adding polymer to coexisting liquid phases with various MWs at various concentrations causes change in T_c , β , and ϕ_c . These changes were confirmed by the ρ measurements in the critical region of IW system. Our results explicitly elucidate that T_c and β increase when the MW and concentration of polymer are increased in the IW system. Presumably, the PEO preferentially adsorbs the water molecules, since water strongly forms hydrogen bonds with nonbonding oxygen (–O–) orbitals in PEO. Our results show that the addition of a very small amount of PEO (as an impurity) to IW not only changes T_c but also changes β and ϕ_c . In the phase separated region, the critical exponents of PEO in IW are higher than that of pure IW. These observations demonstrate the existence of the critical region of IW modified with the addition of PEO.

■ ASSOCIATED CONTENT

Supporting Information. Coexistence curve data from the temperature dependence of density measurements for IW (mass fraction, x_c of I = 0.3826) with various MWs [$0, 2 \times 10^5, 4 \times 10^5, 6 \times 10^5$, and 9×10^5 g mol^{−1}] and different concentrations [$C = 0.395, 0.796$, and 1.605 mg/cm³] of PEO as a function temperature. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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