

Chapter 2

Phase Behavior of PEG/CO₂ System

Abstract High-pressure processes are widely applied in the polymer industry. Near-critical and supercritical fluids (SCFs) (e.g. scCO₂) are used owing to their easily tunable density, which enhances control of polymer solubility and good separability from polymer. On the other hand, for homogeneously catalytic reaction using polyethylene glycol (PEG) as a solvent, CO₂ can act as a miscibility switch to shift the system from homogeneous at atmospheric conditions to heterogeneous under CO₂ pressure. This allows for extraction of the products into the organic solvent phase and immobilization of the homogeneous catalyst in the PEG phase. Understanding of phase behavior in a biphasic solvent system such as PEG/CO₂, where a chemical reaction takes place in one phase and the products can be extracted to another phase, would be critical for the design of efficient and environmentally friendly reaction and separation process. In this chapter, phase behavior of different PEG/CO₂ systems from 1.13–29.00 MPa CO₂ pressure at 313.15–348.15 K with PEG molecular weights (MWs) in the range of 200–35000 is discussed. Ternary systems such as CO₂/PEG/ethanol, CO₂/PEG/1-pentanol, CO₂/PEG/1-octanol, CO₂/PEG/1, 4-dioxane, CO₂/PEG/acetonitrile and CO₂/PEG/1-octene are also investigated. Phase equilibrium data, solid–liquid–vapor (S–L–V) curve, influence of CO₂ addition on viscosity of PEG, solubility data of CO₂ in PEG or PEG in combination with an organic solvent and so on are explored.

Keywords Carbon dioxide • Polyethylene glycol • Phase behavior • Biphasic solvent system • Supercritical fluids • Phase equilibrium

High-pressure processes have been widely applied in the polymer industry. Near-critical and supercritical fluids (SCFs) are in particular used owing to their easily tunable density, which enhances the control of polymer solubility and their good separability from polymer material [1]. SCF solvents (e.g. scCO₂) offer a potential advantage for separation process. The solubility of different polymeric material in SCFs can be systematically varied by changing operating conditions. Several

authors have studied the solubility of polymers in SCFs, which is relevant to the fractionation of polymers and is influenced by pressure, temperature, and the molar mass of the polymer. Fundamental knowledge about phase behavior like equilibrium data under high-pressure conditions is needed to design and develop supercritical separation processes [2].

PEGs are water-soluble polymers which, due to their physiological acceptance, are used in large quantities in the pharmaceutical, cosmetics and food industries. Hence, recent research has focused on using PEG as a recyclable solvent for numerous homogeneously catalyzed reactions, such as the Heck, Suzuki–Miyaura, and Sonogashira coupling [3–6]. However, these reactions generally use organic solvents during the separation steps, allowing for extraction of the products and immobilization of the catalysts in the PEG phase. Unfortunately, this eliminates the environmentally benign nature of these solvent systems. Therefore, alternative separation methods, such as SCF extraction with benign solvents e. g. scCO₂ have been explored. CO₂ can act as a miscibility switch to shift the system from homogeneous at atmospheric conditions to heterogeneous under CO₂ pressure. This allows for extraction of the products into the organic solvent phase and immobilization of the homogeneous catalyst in the PEG phase [7].

During the past decade, scCO₂ has attracted a great deal of attention as “environmentally benign, inexpensive, and nonflammable alternative” solvent for organic reactions. The low viscosity, near-zero surface tension, relative chemical inertness and high diffusivity of scCO₂ results in negligible competitive adsorption with guest molecules on the host substrate and therefore facilitates solute transfer relative to normal solvents. Furthermore, since CO₂ is a gas at ambient conditions, the tedious drying procedure associated with conventional liquid solvents is circumvented and the product is free of residual solvent upon depressurization [8]. It also has relatively mild critical conditions (critical temperature, $T_c = 304$ K, critical pressure $P_c = 7.38$ MPa) and hence allows processing at moderate temperatures at which thermal degradation does not occur [9]. Understanding of phase behavior in biphasic solvent system such as PEG/CO₂, where a chemical reaction performs in one phase while the products can be extracted to another phase, would be critical for the design of efficient, environmentally friendly reaction and separation process.

2.1 Phase Behavior of Different PEG/CO₂ System

High-pressure phase equilibria of PEG/CO₂ systems was investigated by Gulari et al. [10] for the first time, in which the equilibrium phase compositions of different average molecular weight (MW) PEG/CO₂ systems are modeled by using an equation of state (EOS) based on a lattice model. The experimental data cover a range of pressures from 1.13 up to 29.00 MPa at 313 and 323 K. The solubility of PEG in scCO₂ is a strong function of MW. At a fixed temperature and pressure, the solubility of PEGs in CO₂ drops with MW and the threshold pressure above which

the solubility of PEG is detectable increases with MW, for example, 10 MPa for PEG400 and 15 MPa for PEG600. The solubility of CO₂ in PEG varies linearly with pressure, while at pressures above the threshold pressure, it remains relatively constant. The solubility of CO₂ in the liquid polymer phase drops with temperature for both PEG400 and PEG600 because CO₂, which is a volatile component, evaporates out of the liquid phase very effectively with an increase in temperature. In the SCF phase, the solubility of PEG in CO₂ highlights the effect of two competing factors: polymer vapor pressure and SCF density. For example, temperature increasing from 313 to 323 K does not affect the solubility of PEG400 in CO₂, which indicates that increase of vapor pressure of the solute and decrease of the CO₂ density are compensating each other. On the other hand, the solubility of PEG600 in CO₂ falls with temperature, which is governed by decrease in the CO₂ density or its solvation power, because PEG600 with higher MW has a lower vapor pressure.

The experimental phase equilibrium data for three systems PEG200/CO₂, PEG400/CO₂ and PEG600/CO₂ are measured at 313.15, 333.15 and 348.15 K in the range of 3.87–24.87 MPa CO₂ pressure [11]. A trend is shown by the PEG400/CO₂ and PEG600/CO₂ systems: at constant temperature, the respective solubilities increase with pressure; and at constant pressure, the respective solubilities decrease with temperature. In the CO₂-rich phase, the solubility of PEGs increases slightly with pressure, but it is always very low in a pressure range of 0–26 MPa. An increase in temperature or in PEG molar mass reduces the solubility. Qualitatively, the solubility of a polymer in SCFs decreases with the degree of polymerization. In the PEG-rich phase, the CO₂ solubility increases significantly with pressure, especially at low temperature.

The solubilities of CO₂ in PEG400 and PEG600 are very similar at each temperature and pressure, while they are higher than the solubility in PEG200. This low solubility of CO₂ in PEG200 can be attributed to negative end-group effects. Indeed, the properties of low molar mass PEG in solution depend to a large extent on the presence of hydroxyl end groups, which are responsible for attractive interactions such as aggregation and auto-association in the presence of aqueous and organic solvents [12, 13]. However, for PEG/CO₂ systems the influence of hydroxyl end groups becomes negligible when the polymer mass is higher than 400 g mol⁻¹ [14].

PEGs with up to a molar mass of 600 g mol⁻¹ are liquid, while those with higher molar masses are solid. S–L–V transitions for PEG (with MW of 1,500, 4,000, 8,000 and 35,000 g mol⁻¹) are investigated [15]. Generally, applying static pressure to a substance in most cases results in an increase in the melting temperature (S–L transition under pressure). However, for PEG1500, PEG4000 and PEG35000, the liquefaction temperature increases as CO₂ pressure rises to about 10 bar as compared to the melting point at 1 bar; while at pressures greater than 10 bar, the transition temperature of the PEGs investigated decreases (for PEG1500, from 46.2 °C at 1 bar to 30 °C at 70 bar) due to the effect of CO₂ molar volume under different hydrostatic pressure. For V–L transition, the solubility of

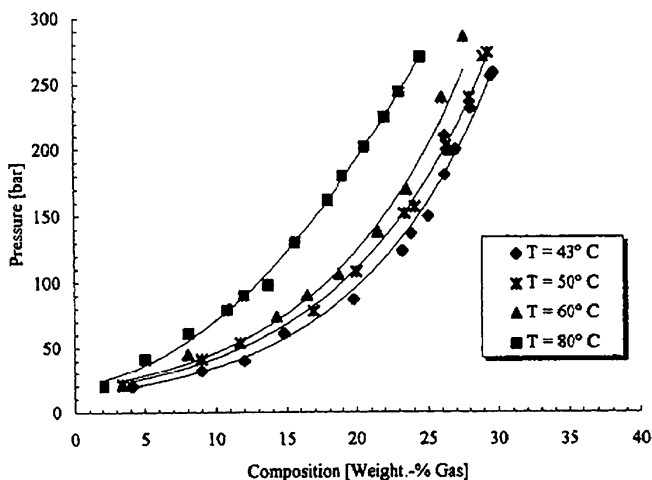


Fig. 2.1 Solubility of CO₂ in PEG1500 at various temperatures and pressures. (Reprinted from Ref. [15], with permission from Elsevier)

CO₂ in PEG1500 decreases with increasing temperature, and increases with increasing pressure (Fig. 2.1).

Influence of SCF addition on polymer properties (density and viscosity) is measured in a range of temperatures from 313 to 348 K and at pressures up to 25 MPa [16]. For the CO₂-saturated PEG400 at 313.25, 332.89 and 347.77 K, a minimum viscosity of about 5 MPa s at 25 MPa is obtained at 313.25 K, corresponding to 89 % viscosity reduction. At 332.89 K this viscosity reduction is about 83 %, and at 347.77 K it is only 76 %. This phenomenon can be related to a decrease of the CO₂ solubility in the PEG400 when temperature increases. For densities of PEG400, it increases rapidly with CO₂ pressure in the low-pressure region ($P < 3$ MPa).

Phase equilibria in the binary polymer/gas systems such as PEG/propane, PEG/N₂ and PEG/CO₂ have been investigated, with PEG MW of 200, 1,500, 4,000 and 8,000 g mol⁻¹, in a temperature range of 50–120 °C and a pressure range from 5 to 300 bar using a static-analytical method [17]. It is found that CO₂ dissolves much better in PEG than does propane or N₂. With rising temperature, the PEG/CO₂ miscibility gap increases, whereas the miscibility gaps of the PEG/propane and the PEG/N₂ systems decrease. The influence of the polymer MW on the gas solubility is almost negligible for PEG1500–PEG8000, while the behaviour of the small PEG200 deviates significantly due to strong endgroup influence.

Understanding of phase behavior in biphasic systems such as PEG/CO₂ is critical for the design of an efficient and environmentally friendly reaction and separation process. Jessop et al. developed the first PEG/scCO₂ scheme in the rhodium catalyzed hydrogenation of styrene to ethyl benzene, in which the reaction is conducted at 40 °C and then swept with scCO₂ to remove the products, and the catalyst is immobilized in the PEG phase and recycled five times with no loss

in activity [18]. As previously reported, the solubility of PEG in scCO₂ can be dramatically reduced by increasing the temperature and by increasing the MW of PEG. Increasing the temperature of scCO₂ decreases in the solubility of PEG, while raises the solubility of typical organic small molecule products [19]. Commercially available PEG1500 is found to be a waxy solid at room temperature, melting at 48–51 °C, but a liquid at 40 °C if it is under a CO₂ pressure of greater than 90 bar. Thus, PEG1500 is chosen as solvent for scCO₂ extraction of ethylbenzene, with less co-extracted PEG (0.2 mg, 0.1 %), than the case with PEG900. Commercially available PEG fractions with average MWs of 300 and 600 are viscous liquids at room temperature but are readily extracted by scCO₂.

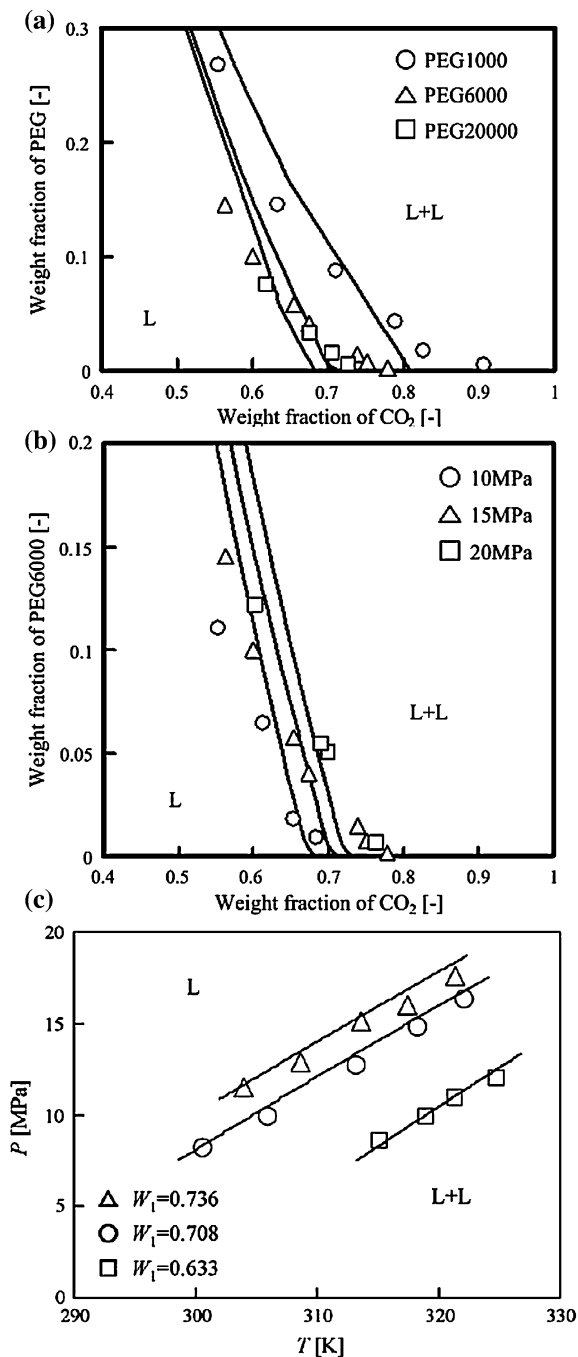
2.2 Phase Behavior of PEG/CO₂/Organic Solvent

In the polymer industry involving SCFs, a co-solvent is commonly needed because the solubility of a polymer in high-pressure is very low. In order to consider an effective method for the production of polymeric materials using scCO₂, it is essential to understand the liquid–liquid (L–L) phase behavior of CO₂ + polymer + co-solvent systems at constant pressure and temperature [9, 20].

A mixture of CO₂ + PEG + ethanol splits into two liquid phases at 15 MPa and 313.2 K: a polymer-rich phase and a polymer-lean phase [9]. The solubility of PEG in the polymer-lean (CO₂-rich) phase is very low (less than 1 wt. %) because CO₂ behaves as a non-solvent for PEGs. On the other hand, in the polymer-lean phase, the solubility of PEG increases with an increase in ethanol concentration because ethanol is a relatively good solvent for PEG at 313.2 K. In the L–L phase boundary of the PEG + CO₂ + ethanol system, the size of the two-phase region increases with an increase in the PEG MW from 1000 to 20000 at 313.2 K and 15 MPa (Fig. 2.2a). The effect of pressure (from 10 to 20 MPa) on the cloud point (cloud point of a fluid is the temperature at which dissolved solids are no longer completely soluble, precipitating as a second phase giving the fluid a cloudy appearance) of the CO₂ + PEG6000 + ethanol system at 313.2 K shows that the L–L boundary region decreases with increasing pressure (Fig. 2.2b), due to the increase of solvent density, resulting in the enlargement of the one phase region. When the ethanol to PEG6000 weight ratio is 95:5, the L–L boundary pressure increases with temperature (Fig. 2.2c), owing to the relatively rapid expansion of the solvent with increasing temperature, which makes it a less good solvent at higher temperatures [21]. The cloud point pressure increases with increasing in CO₂ concentration, and CO₂ enlarges the two-phase region. The addition of CO₂ to ethanol causes a lowering of the dissolving power of the mixed solvent.

The solubility of CO₂ in 1-pentanol, 1-octanol, PEG200, PEG200 + 1-pentanol and PEG200 + 1-octanol mixtures at 303.15, 313.15 and 323.15 K at pressures up to 8 MPa are measured, and the mass ratios of PEG200 to the alcohols are 1:0, 3:1, 1:1, 1:3 and 0:1, respectively [22]. The solubility of CO₂ in the neat solvents and the mixed solvents with different compositions increases with increasing pressure

Fig. 2.2 **a** Effect of the MW of PEG on the cloud point compositions of the CO₂ (1) + PEG (2) + ethanol (3) system at 313.2 K and 15 MPa. **b** Effect of pressure on the cloud point compositions of the CO₂ (1) + PEG (2) + ethanol (3) system at 313.2 K. **c** Cloud point pressures of the CO₂ (1) + PEG (2) + ethanol (3) system. The ethanol to PEG6000 weight ratio is 95:5. Symbols are experimental cloud point compositions. Solid lines are determined using the Sanchez-Lacombe EOS. (Reprinted with permission from Ref. [9], with permission from Elsevier)



of CO₂. The solubility of CO₂ in 1-pentanol and 1-octanol is larger than that in PEG200, and the solubility of CO₂ in the mixed solvents increases with increasing weight percent of 1-pentanol or 1-octanol. The solubility of CO₂ in PEG200 + 1-pentanol is larger than that in PEG200 + 1-octanol, because CO₂ is more soluble in 1-pentanol than that in 1-octanol. In addition, an increase in temperature results in decrease in the solubility of CO₂.

Phase behavior for PEG400 and CO₂ with 1,4-dioxane and acetonitrile at 25 and 40 °C is explored, in which two liquid phases, a PEG-rich lower and an organic-rich upper, as well as a CO₂-rich vapor phase are showing [7]. For the PEG400/1,4-dioxane/CO₂ system at 25 °C, with CO₂ pressure increasing from 5.2 to 6.0 MPa, the compositions in the PEG-rich phase show increasing PEG content with decreasing amounts of both CO₂ and dioxane. The dioxane-rich phase shows a modest decrease in PEG content and significant increase in CO₂. The increase in CO₂ causes the dioxane content to decrease, which allows CO₂ to enhance its lead as the primary component of the second liquid phase at >90 wt %. For the EPG400/acetonitrile/CO₂ system at 25 °C with CO₂ pressure increasing from 5.5 to 6.2 MPa, the compositions in the PEG-rich phase show a minimal change in the PEG content, with increasing CO₂ and decreasing acetonitrile. The acetonitrile-rich phase shows decreasing PEG and acetonitrile with increasing CO₂.

For vapor–liquid equilibria for CO₂ + 1-octene + PEG at 308.15, 318.15 and 328.15 K at pressures up to 10 MPa, with PEG MWs of 200, 400 and 600, three-phase region of the ternary systems exists: a CO₂-rich phase, a 1-octene-rich phase and a PEG-rich phase [23]. The solubility of PEGs in 1-octene and in CO₂ is extremely low. Mass fraction of 1-octene increases with increasing pressure in the low-pressure range and decreases with an increase in pressure in the high-pressure region, because pressure affects the mass fraction in two opposite ways: first, the increase of pressure should enhance the dissolution of 1-octene because CO₂ reduces the PEG polarity, and the concentration of CO₂ in the PEG-rich phase increases with increasing pressure; second, an increase in pressure results in an increase in the solvent power of CO₂ in the vapor phase, which is unfavorable to the dissolution of 1-octene in the PEGs. The competition of the two factors results in the maxima in the curves. So the solubility of 1-octene in PEGs can be enhanced considerably by CO₂ at suitable pressures. For reactions involving olefins, the low solubility of the olefin in PEGs may lower reaction rates, reduce product yields and cause the reaction to be mass-transfer limited. This disadvantage can be overcome to a certain degree by adding CO₂. In addition, dissolution of CO₂ may reduce the viscosity because dissolution of CO₂ can reduce the viscosity of other liquids significantly, which may also enhance the reaction rate [24]. The mass fraction of 1-octene in the PEG-rich phase increases with increasing PEG MW. This is understandable that the polarity of a PEG with larger MW is lower, while 1-octene is non-polar. An increase in temperature results in an increase in mass fraction of 1-octene in the PEG-rich phase, originating from the higher solubility of 1-octene in the PEGs at higher temperature. The mass fraction of CO₂ in the PEG-rich phase increases continuously with increasing pressure, or increasing temperature at all the pressures and also with the increase of PEG MW.

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