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Phase behavior of tetrahydrofurfuryl methacrylate and poly (tetrahydrofurfuryl methacrylate) in supercritical carbon dioxide

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ABSTRACT

High pressures phase behavior data for the CO_2/tetrahydrofurfuryl methacrylate (THFMA) systems are presented at (313.2–393.2) K and up to 22.07 MPa. The system exhibits the Type-I phase behavior with a continuous mixture-critical curve. The solubilities of poly(tetrahydrofurfuryl methacrylate) [P(THFMA)] + THFMA or dimethyl ether (DME) in supercritical carbon dioxide (CO_2) were measured up to 490.5 K and 289.83 MPa. The cloud-point pressure for the P(THFMA) + CO_2 system shifts to lower pressures as adding THFMA and DME as a cosolvent. P(THFMA) in pure CO_2 did not dissolve up to the temperature of 498 K and pressure of 300.0 MPa. All experimental results with vapor-liquid equilibrium (VLE) for the CO_2/THFMA binary system and the cloud-point phase behaviors for the P(THFMA)/CO_2/cosolvent ternary systems were adequately modeled by the PC-SAFT equation of state. Calculation of the results with the PC-SAFT model showed that the UCST-type phase behavior is mainly due to governed by the interaction between the same species (i.e., between THFMA and THFMA, and between CO_2 and CO_2), rather than that between different species (i.e., between THFMA and CO_2).

1. Introduction

In the polymer and related industrial processes, environmentally friendly process is becoming an important factor to consider. Various supercritical fluid (SCF) solvents have been examined as media for polymerization processes, polymer purification, solution coatings and fractionation [1–4]. High-pressure carbon dioxide (CO_2) in polymer processing has been used as a viscosity modifier, plasticizing agent, foaming agent, and reaction medium [5–7]. CO_2 as a supercritical solvent is inexpensive, sustainable, relatively benign, and environmentally-friendly. The addition of CO_2 to polymer systems has a profound effect on their thermodynamic properties (e.g., solubility and cloud-point pressure) and phase behavior, such as upper critical solution temperature (UCST), and lower critical solution temperature (LCST). Most polymers are not easily soluble in CO_2, but the addition of monomer with liquid state as a cosolvent leads to great enhancement of polymer solubility in the supercritical fluid at lower temperatures and lower pressures. Solubility is one of the fundamental properties in understanding the phase behavior of multicomponent mixtures. The physical properties of polymers are usually affected by the type and amount of low molecular-weight components. As a result, the attention has been placed on the experimental and theoretical research into the phase behavior of polymer systems and monomer in supercritical fluids. Furthermore, the thermodynamic understanding of the pressure-composition curves of repeating units (i.e., monomer) of polymer in the SCF CO_2 has been essential in new plant design in various fields [8–12]. Until recently, (meth)acrylate-based polymers have been widely used in the plastic technology fields. Polymers with (meth)acrylate type monomer are mainly used for a variety of applications such as glazing, medicine, optics, oil additives, building materials, and the toy industry [13]. Many experimental studies for (meth)acrylate-based copolymers in SCF CO_2 conditions have been published over the last two decades. [14–17] In particular, the dispersion polymerization is applied to the formation of micelles in CO_2 medium, where the micellar core is CO_2-phobic, and the CO_2-philic shell extends into the solvent.

In this work, the phase behaviors at high pressure was experimentally investigated for binary and ternary mixture containing polymer with tetrahydrofurfuryl methacrylate (THFMA) repeating unit in SCF CO_2 with cosolvents (i.e., dimethyl ether (DME) and THFMA monomer). Poly(tetrahydrofurfuryl methacrylate) [P(THFMA)] has been investigated as a biomaterial for encouraging articular cartilage repair, because that it possesses some unique characteristics with respect to its biocompatibility and behavior in water [18]. Furthermore, its monomer was used as a tissue repair material [19,20]. In addition, the critical-point (CP), bubble-point (BP), and dew-point (DP) pressures for the CO_2/THFMA system were measured at temperatures in the

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range of (313.2–393.2) K and at pressures up to 22.07 MPa. For further theoretical investigation, the PC-SAFT [21] equation of state (EoS) was applied to describe their phase behaviors, and reasonable calculation results were obtained.

2. Theoretical background

In the PC-SAFT EoS by Gross and Sadowski [21,22], the molecule is considered as a flexible chain with several hard-spherical segments. The compressibility factor $Z = Pv/(RT)$ for non-associating molecule is expressed as

$$Z^{PC-SAFT} = 1 + (\overline{m}Z^{hs} + Z^{chain}) + Z^{disp} \tag{1}$$

where *hs*, *chain* and *disp* indicate the hard-sphere, chain and dispersive term, respectively. The hard-sphere contribution describes the repulsive force between hard-spherical segments.

$$Z^{hs} = \frac{\xi_3}{(1-\xi_3)} + \frac{3\xi_1\xi_2}{\xi_0(1-\xi_3)^2} + \frac{3\xi_2^3-\xi_3\xi_2^3}{\xi_0(1-\xi_3)^3} \tag{2}$$

where ξ_n is the function of ρ (molar density) and is defined as follows:

$$\xi_n = \frac{\pi}{6}\rho\sum_i x_i m_i d_{ii}^n \quad n \in 0,\ 1,\ 2,\ 3 \tag{3}$$

where x_i is the mole fraction and m indicates the number of segments. As well, d is the temperature-dependent diameter and is expressed as follows:

$$d_{ii}(T) = \sigma_{ii}[1-0.12\exp(-3\varepsilon_{ii}/kT)] \tag{4}$$

where σ is the segment diameter and ε/k is the dispersion energy parameter between chain-like molecules. The chain term describes the contribution of the chain connectivity between the same segments.

$$Z^{chain} = \sum_i x_i(1-m_i)(g_{ii}^{hs})^{-1}\rho\frac{\partial g_{ii}^{hs}}{\partial\rho} \tag{5}$$

where g_{ij}^{hs} is the radial distribution function, which is defined as

$$g_{ij}^{hs} = \frac{1}{1-\xi_3} + \frac{d_{ii}d_{jj}}{d_{ii}+d_{jj}}\frac{3\xi_2}{(1-\xi_3)^2} + \left(\frac{d_{ii}d_{jj}}{d_{ii}+d_{jj}}\right)^2\frac{\xi_2^2}{(1-\xi_3)^3} \tag{6}$$

The dispersion term is written for hard-chains of segments and expresses all attractive interactions among molecules.

$$Z^{disp} = Z_1^{disp} + Z_2^{disp} \tag{7}$$

$$Z_1^{disp}/NkT = -2\pi\rho\frac{\partial(\eta I_1)}{\partial\eta}\sum_i\sum_j x_i x_j m_i m_j(\varepsilon_{ij}/kT)\sigma_{ij}^3 \tag{8}$$

$$Z_2^{disp}/NkT = -\pi\rho\overline{m}\left[C_1\frac{\partial(\eta I_2)}{\partial\eta} + C_2\eta I_2\right]\sum_i\sum_j x_i x_j m_i m_j(\varepsilon_{ij}/kT)^2\sigma_{ij}^3 \tag{9}$$

All parameters in each term are described in detail in the literature [21,22].

The mixing rule for the characteristic parameters σ_{ij} and ε_{ij} between unlike segments is given by

$$\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j) \tag{10}$$

$$\varepsilon_{ij} = (1-k_{ij})\sqrt{\varepsilon_{ii}\varepsilon_{jj}} \tag{11}$$

where k_{ij} is a mixture parameter that accounts for specific binary interaction between components i and j.

3. Experimental section

3.1. Materials

Table 1 gives the specifications of the polymer and monomer used in this work that were purchased from Scientific Polymer Products Inc.. The purchased P(THFMA) was purified under vacuum for at least 10 h in the Rotary evaporator (Buchi UK Ltd., Rotavapor R-205), to remove toluene. The molecular weight (M_w) of P(THFMA) is 240,000 g/mole. The THFMA, DME, and CO_2 were used as received, without further purification. To prevent the polymerization of THFMA monomer, the inhibitor (i.e., 2,6-di-tert-butyl-4-methyl phenol, Aldrich, purity > 99.0 wt.%) was used at a concentration of 0.005 times of the THFMA amount. Fig. 1 shows the molecular structure for P(THFMA) and THFMA.

Table 1
Specifications of the chemical used.

Chemicals	Source	Mass Fraction Purity[a]	Purification Method	Analysis Method[a]
CO_2	Deok Yang Gas Co.	> 0.999	None	–
DME[d]	E1 Co.	> 0.995	None	–
THFMA[f]	Scientific Polymer Products, Inc.	> 0.980	None	GC[b]
P(THFMA)[h]	Scientific Polymer Products, Inc.	M_w = 240,000	None	GPC[c]

[a] Both the analysis method and the mass fraction purity were provided by the suppliers.
[b] Gas chromatography.
[c] Gel permeation chromatography.
[d] DME = Dimethyl ether.
[f] THFMA = Tetrahydrofurfuryl Methacrylate ($C_9H_{14}O_3$, M_w = 170.21, CAS RN 2455-24-5).
[h] P(THFMA) = Poly(tetrahydrofurfuryl methacrylate) (CAS RN 25035-85-2).

3.2. Apparatus

Fig. 2 shows the typical variable-volume view cell, which is described in detail elsewhere [23–26]. The high-pressure view cell apparatus, consisting of generator, pressure gauge and borescope (Olympus Corp., F100-038-000-50) is used to measure the various phase behaviors. The contents in the view cell are compressed to the desired operating pressure by displacing an internal piston (2.54 cm length), using water pressurized with a high-pressure generator (for polymer system: HIP 37-5.75-60; for monomer system: HIP 68-5.75-15). The pressure of systems was determined using a Heise gauge (for monomer system: Dresser CM-53920, 0– 34.0 MPa, standard uncertainty of 0.03 MPa; for polymer system: Dresser CM-108952, 0–345.0 MPa, standard uncertainty of 0.35 MPa). A thick sapphire window, which is fitted to one end of the view cell and is sealed with an O-ring, enables direct visual observation of the phase behavior. The contents of the view cell are projected onto a video monitor using a camera coupled to a borescope placed directly against the sapphire window. With this technique, it was possible to easily and clearly observe the cloud point and determine the composition of the newly formed phases as a function of pressure. The experimental procedure for BP, DP, CP and cloud-point is described in detail elsewhere [23,27–31]. The uncertainties of the experimental system are caused by the measurement of temperature (T), pressure (p), and composition (x). The uncertainties of T, p and x can be calculated by the repeatability ($u_{x_{rep}}(f)$), resolution ($u_{x_{res}}(f)$), and correction ($u_c(f)$) [32,33]. The standard uncertainty of the arbitrary f function is:

$$f = x + c \tag{12}$$

where, x is the measured value, and c is the correction value.

$$u_f^2 = \left(\frac{\partial f}{\partial x}u_x\right)^2 + \left(\frac{\partial f}{\partial c}u_c\right)^2 = u_{x_{rep}}^2(f) + u_{x_{res}}^2(f) + u_c^2(f) \tag{13}$$