The Journal of Supercritical Fluids 135 (2018) 211–217

Contents lists available at ScienceDirect

The Journal of Supercritical Fluids

journal homepage: www.elsevier.com/locate/supflu

Solubility on tetrahydrofurfuryl acrylate effect for the poly [tetrahydrofurfuryl acrylate] in supercritical carbon dioxide and dimethyl ether

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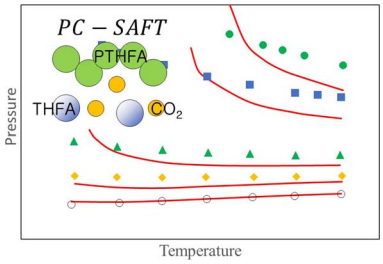
GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Supercritical fluid
Poly(tetrahydrofurfuryl acrylate)
Tetrahydrofurfuryl acrylate
Carbon dioxide
Cloud-point curve

ABSTRACT

In this work, the phase behavior for a binary and ternary mixture of polymer with a tetrahydrofurfuryl acrylate (THFA) repeating unit in supercritical conditions were investigated experimentally and theoretically. High-pressure solubility data for the THFA in supercritical carbon dioxide (CO_2) fluid were presented over a broad temperature range from 313.2 K to 393.2 K and up to a pressure of 21.86 MPa. The cloud-point measurements in binary and ternary mixtures for poly(tetrahydrofurfuryl acrylate) [PTHFA] + THFA or dimethyl ether (DME) in supercritical CO_2 were carried out up to 456.2 K and 255.34 MPa. When THFA and DME were added as co-solvents the cloud-point for PTHFA + CO_2 fluid shifted a lower pressure. The PC-SAFT model was applied to describe the phase behavior for all experimental results, which were adequately modeled. Through theoretical investigation with the PC-SAFT model, it was found that the strong interaction between polymer and CO_2 causes wide one fluid for the PTHFA/CO_2/THFA system, and the interactions between CO_2 and DME molecules have strong effects on the phase behavior for the PTHFA/CO_2/DME system.

1. Introduction

The thermodynamic property information at high pressure for the multicomponent mixtures composed of polymer, supercritical fluid (SCF) solvent, and cosolvent components plays an important role in the basic understanding and design for various polymer processes, particle preparation technology, and separation processes [1–4]. Polymer processing using high-pressure carbon dioxide (CO_2) has attracted attention for many applications such as synthesis, extraction and particle generation [5–7]. Due to such reasons, the experimental studies for polymer processes under SCF conditions have been of major interest [8,9]. Also, the thermodynamic understanding of the pressure-composition curves of the repeating unit (i.e., monomer) of the polymer in the SCF CO_2 has been essential in the new plant design [10–14]. Dimethyl

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https://doi.org/10.1016/j.supflu.2018.01.026
Received 10 October 2017; Received in revised form 19 January 2018; Accepted 26 January 2018

ether (DME) has been used as a solvent under SCF conditions and has also been investigated as a refrigerant [15,16], a mobile phase in chromatographic applications [17] and as an alternative fuel.[18] In general, the polymer does not dissolve easily into the solvent, but better solubility is shown in the supercritical fluid. The CO_2 and DME have been popularly used as good solvents under supercritical condition for many polymers. Up to now, the acrylate-based polymers are widely used from lower strength to a higher-strength plastic technology. The methacrylate-based polymers are mainly used for various applications such as glazing, medicine, optics, oil additives, building materials and the toy industry [19]. In particular, poly(tetrahydrofurfuryl acrylate) [PTHFA] is used as a component in adhesives and sealants, in photosensitive chemicals and in biomedical materials [20].

The main goal in this work is to investigate the phase behavior for binary and ternary mixtures of the polymer, with tetrahydrofurfuryl acrylate (THFA) as a repeating unit in supercritical CO_2 + dimethyl ether (DME) and in the supercritical CO_2 + THFA monomer. In addition, the critical-point (CP), bubble-point (BP) and dew-point (DP) pressures for the CO_2 + THFA are measured over wide temperature and high pressure ranges. For further theoretical investigations, all measured experimental results are modeled by PC-SAFT equation of state (EoS) [21] which is suitable to correlate and predict various phase behaviors [22,23].

2. Theoretical background

In the PC-SAFT EoS developed by Gross and Sadowski [21,24], the molecule is assumed as a flexible chain composed of several hard-spherical segments. The compressibility factor for non-associating molecule is expressed as

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

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

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

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

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

where x_i is the mole fraction, and m indicates the number of the segments. Additionally, the d is the temperature-dependent diameter and is expressed as following

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

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.

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

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

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

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

$$Z^{disp} = Z_1^{disp} + Z_2^{disp} \quad (7)$$

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

Table 1
Specifications of chemicals used in this study.

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	–
THFA[e]	Scientific Polymer Products, Inc.	> 0.950	None	GC[b]
PTHFA[g]	Scientific Polymer Products, Inc.	M_w = 150,000	None	GPC[c]

[a] Analytical method and the mass fraction purity are provided by the suppliers.
[b] Gas chromatography.
[c] Gel permeation chromatography.
[d] DME = Dimethyl ether.
[e] THFA = Tetrahydrofurfuryl acrylate ($C_8H_{12}O_3$, M_w = 156.18, CAS RN 2399-48-6).
[g] PTHFA = Poly(tetrahydrofurfuryl acrylate) (CAS RN 29324-52-5).

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

All parameters in each term are described in detail in the literature [21,24].

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

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

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

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

3. Experiment

3.1. Materials

All chemicals used in this work are purchased from Scientific Polymer Products Inc., and their specifications are given in Table 1. The PTHFA in toluene was placed under vacuum for at least 10 h in the Rotary evaporator by Buchi UK Ltd (Rotavapor R-205) to remove toluene. The solvent, DME and CO_2 were used as received without further purification. To prevent the polymerization of THFA, 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 amount of THFA. The molecular structures for PTHFA and THFA are shown in Fig. 1.

3.2. Apparatus

The typical variable-volume view cell is described in detail elsewhere [25–27] and is used to measure the cloud-point, CP, DP and BP. It consists of the high-pressure generator, pressure gauge, variable-volume view cell and borescope (Olympus Corp., F100-038-000-50). The solution in the cell was 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 solution: HIP 37-5.75-60; for monomer solution: HIP 68-5.75-15). The experimental data in the mixture was determined using a Heise gauge (for the monomer solution: Dresser CM-53920, 0 ~ 34.0 MPa, the standard uncertainty of 0.03 MPa; for polymer solution: Dresser CM-108952, 0 ~ 345.0 MPa, the standard uncertainty of 0.35 MPa). The thick sapphire window, which is fitted to one end of the view cell and is sealed with an O-ring, enables the direct visual observation of the phase behavior. The contents of the view cell are projected onto a video monitor using a camera