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Bubble-point measurement for the binary mixture of propargyl acrylate and propargyl methacrylate in supercritical carbon dioxide

Seung-Hyun Baek, Hun-Soo Byun *

Department of Chemical and Biomolecular Engineering, Chonnam National University, Yeosu, Jeonnam 59626, South Korea

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Acrylate and methacrylate (acrylic acid type) are compounds with weak polarity which show a non-ideal behaviour. Phase behaviour of these systems play a significant role as organic solvents in industrial processes. High pressure phase behaviour data were reported for binary mixture of propargyl acrylate and propargyl methacrylate in supercritical carbon dioxide. The bubble-point curves for the (carbon dioxide + propargyl acrylate) and (carbon dioxide + propargyl methacrylate) mixtures were measured by static view cell apparatus at temperature range from 313.2 K to 393.2 K and at pressures below 19.14 MPa. The (carbon dioxide + propargyl acrylate) and (carbon dioxide + propargyl methacrylate) systems exhibit type-I phase behaviour. The (carbon dioxide + (meth)acrylate) systems had continuous critical mixture curves with maximums in pressure located between the critical temperatures of carbon dioxide and propargyl acrylate or carbon dioxide and propargyl methacrylate. The solubility behaviour of propargyl (meth)acrylate in the (carbon dioxide + propargyl acrylate) and (carbon dioxide + propargyl acrylate) systems increases as the temperature increases at a fixed pressure. The experimental results for the (carbon dioxide + propargyl acrylate) and (carbon dioxide + propargyl methacrylate) systems correlate with the Peng–Robinson equation of state using a van der Waals one-fluid mixing rule. The critical properties of propargyl acrylate and propargyl methacrylate were predicted with the Joback–Lyderson group contribution and Lee–Kesler method.

1. Introduction

Acrylate and methacrylate monomers are used as building blocks to make a wide range of polymers [1]. The polymers are used as raw materials of components in the preparation of a wide range of formulations or objects that are used in our everyday life, especially when stability, durability, hardness and scratch resistance are needed. Propargyl (meth)acrylate are characterised by a wide variety of applications such as adhesives, chemical intermediates, coatings, leather, plasticizers, plastics and textiles [2,3].

The phase equilibria of binary system consisting of (meth)acrylate with supercritical carbon dioxide play an very important role in chemical industry, separation process, polymer processes, and related industrial applications [4–6]. Supercritical carbon dioxide has a quadrupole moment, no dipole moment, and low dielectric constant [7], so it has been recommended as the solvent chosen for many industrial applications because it is an environmentally benign, non-hazardous, inexpensive, and non-toxic solvent with a nonpolar molecule.

The experimental values for the binary mixture of solute monomer in supercritical carbon dioxide have been reported on the bubble-point, dew-point and critical-point phase behaviour [8,9]. Therefore, knowledge of thermodynamic properties of (carbon dioxide + solute) mixtures is required for practical uses in chemical processes. Phase behaviour on miscibility for the {carbon dioxide + (meth)acrylate} mixture is an important condition needed for polymerization process and synthesis. However, (vapour + liquid) equilibria data for the (carbon dioxide + (meth)acrylate) mixtures were reported by Cho *et al.* [10], Jeong and Byun [11], Gwon *et al.* [12], Yoon *et al.* [13] and Yang *et al.* [14]. Cho *et al.* [10] measured the (vapour + liquid) curves for the (carbon dioxide + 2-ethoxyethyl methacrylate) and (carbon dioxide + 2,3-epoxypropyl methacrylate) systems at temperatures ranging from (313.2 to 393.2) K and pressure up to 21.3 MPa with a static method by using high pressure apparatus. The phase behaviour for the (carbon dioxide + isobornyl methacrylate) system reported by Jeong and Byun [11] was about a binary mixture at temperatures ranging from (313.2 to 393.2) K and pressures ranging from (3.29 to 23.52) MPa. Gwon *et al.* [12] reported the phase equilibrium for the (carbon dioxide + tetrahydrofurfuryl acrylate) and (carbon dioxide + tetrahydrofurfuryl methacrylate) systems at

* Corresponding author. Tel.: +82 61 659 7296; fax: +82 61 653 3659.
E-mail address: hsbyun@jnu.ac.kr (H.-S. Byun).

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temperatures of (313.15, 323.15, 333.15, 343.2, 353.2 and 363.2) K and pressures between 5.15 MPa and 17.70 MPa by using a variable-volume view cell. Yoon *et al.* [13] reported the experimental results for the binary system for the (carbon dioxide + heptafluorobutyl (meth)acrylate) systems at temperatures from (313.2 to 393.2) K and pressures up to 14.30 MPa. Yang *et al.* [14] measured the solubility of isobornyl acrylate in supercritical carbon dioxide within the temperature range of (313.2 to 393.2) K and pressure ranging of (4.05 to 22.86) MPa.

The purpose of this work is to obtain the phase equilibria data at elevated pressure and temperatures for the (carbon dioxide + propargyl acrylate) and (carbon dioxide + propargyl methacrylate) mixtures. The experimental values for the (carbon dioxide + propargyl acrylate) and (carbon dioxide + propargyl methacrylate) systems obtained in this work were correlated with the Peng–Robinson equation of state [15] using a van der Waals one-fluid mixing rule that contains two adjustable parameters (k_{ij}, η_{ij}). The critical pressure, critical temperature and acentric factor of propargyl acrylate and propargyl methacrylate are estimated by the Joback and Lydersen method with group contributions [16].

2. Experimental

2.1. Materials

Propargyl acrylate (>0.980 mass fraction purity; $CH_2{=}CHCOOCH_2C{\equiv}CH$) and propargyl methacrylate (>0.980 mass fraction purity; $CH_2{=}C(CH_3)COOCH_2C{\equiv}CH$) used in this work were obtained from Polysciences, Inc. Both components were used without further purification in the experiments. Carbon dioxide (>0.999 mass fraction purity) was obtained from Deok Yang Co. and used as received. The specifications of all chemicals used are summarized in table 1.

2.2. Apparatus and procedure

The experimental apparatus (see figure 1) and techniques used to measure the phase behaviour of propargyl (meth)acrylate monomers in supercritical carbon dioxide are described in detail elsewhere [17,18]. A variable-volume view cell was used to measure the phase behaviour that operated pressures up to 200.0 MPa. Typically, supercritical carbon dioxide was added to the cell to within ±0.002 g using a high pressure bomb. After the empty cell was purged several times with carbon dioxide and nitrogen to remove traces of air and organic matter, the monomer was loaded into the cell to within ±0.0008 g using a syringe. The piston (2.54 cm length) was moved using water pressurised by a high pressure generator (HIP, model 37-5.75-60). Pressure of the mixture was measured with a Heise gauge (Dresser Ind., model CM-53920, 0 to 34.0 MPa) accurate to within ±0.02 MPa. The temperature of the cell, typically maintained to within ±0.2 K, was measured by a platinum-resistance thermometer (Thermometrics Corp., Class A) and a digital multimeter (Yokogawa, model 7563, accurate to ±0.005%). The mixture inside the cell can be seen on a video monitor using a camera coupled to a borescope (Olympus Corp., model F100-038-000-50) placed against the outside of the sapphire window.

To measure for bubble point, dew point and mixture-critical point, to be measured a bubble point pressure was obtained when small vapour bubbles appeared in the cell, while a dew point was obtained after appearance of a fine mist. The solution in the cell was compressed to a single phase at a fixed temperature. The inside of the solution was maintained in the single phase region at the desired temperature for at least ~40 min to allow the cell to reach phase equilibrium. The pressure was then slowly decreased until a second phase appeared.

3. Results and discussion

Pressure-composition isotherms for the propargyl acrylate and propargyl methacrylate in supercritical carbon dioxide were determined, and the experimental uncertainty is estimated to be ±0.10 MPa and T = ±0.12 K for a given loading of the cell [20,21]. The combined expanded uncertainties of propargyl acrylate and propargyl methacrylate mole fractions are estimated to be ±0.0008 [19].

Figure 2(a) and table 2 explain the experimental pressure-composition (P,x) isotherms at temperatures (313.2, 333.2, 353.2, 373.2 and 393.2) K, and pressures from (5.69 to 24.90) MPa for the (carbon dioxide + propargyl acrylate) system. Three phases were not observed at five temperatures. As shown in figure 2, the mixture critical pressures are 17.01 MPa (at temperature = 373.2 K) and 17.20 MPa (at temperature = 393.2 K). The (P, x) isotherms shown in figure 2 are consistent with those expected for a type-I system [22,23], where a maximum takes place in the mixture-critical curve. The type-I phase diagram is the simplest phase behaviour for a binary mixture. The apparent traits of type-I behaviour are that only a single phase exists throughout the phase diagram and that the mixture critical curve runs continuously from the critical point of the carbon dioxide component to the critical point of the propargyl acrylate component [16]. The solubility of carbon dioxide decreases as temperatures shift higher under a constant pressure.

Figure 2(b) and table 3 show the experimental values at temperatures = (313.2, 333.2, 353.2, 373.2 and 393.2) K, and at pressures from (3.94 to 23.21) MPa for the (carbon dioxide + propargyl methacrylate) mixture. As shown in figure 2(b), the critical mixture pressures are 14.70 MPa (at temperature = 353.2 K), 17.04 MPa (at temperature = 373.2 K) and 19.14 MPa (at temperature = 393.2 K). The (carbon dioxide + propargyl methacrylate) system does not show three phases at the five temperatures investigated.

In this work, the experimental phase behaviour correlate with the Peng–Robinson equation of state. The Peng–Robinson equations are briefly described here. The Peng–Robinson equation of state [15] is expressed as follows:

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)+b(V-b)} \tag{1}$$

$$a(T) = 0.457235\frac{\alpha(T)R^2T_c^2}{p_c} \tag{2}$$

$$b = 0.077796\frac{RT_c}{p_c} \tag{3}$$

TABLE 1
Specifications of the chemicals used in this work.

Chemical name	Mass fraction purity	Molecular formula	Source	CAS RN
Carbon dioxide	>0.999	CO_2	DeokYang Co.	124-38-9
Propargyl acrylate	>0.980	$C_6H_6O_2$	Polysciences	10477-47-1
Propargyl methacrylate	>0.980	$C_7H_8O_2$	Polysciences	13861-22-8