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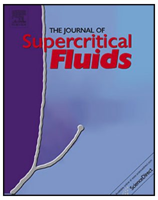

Phase behavior for the poly[2-(2-ethoxyethoxy)ethyl acrylate] and 2-(2-ethoxyethoxy)ethyl acrylate in supercritical solvents

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ABSTRACT

Pressure-composition (p, x) isotherms were obtained for the carbon dioxide + 2-(2-ethoxyethoxy)ethyl acrylate [2-(2-EE)EA] system at five temperatures (313.2 K, 333.2 K, 353.2 K, 373.2 K, and 393.2 K) and pressure up to 22.86 MPa. The carbon dioxide + 2-(2-EE)EA system exhibits type-I phase behavior with a continuous mixture critical curve. The experimental results for carbon dioxide + 2-(2-EE)EA mixtures are correlated using the Peng–Robinson equation of state (PR-EOS) using mixing rule including two adjustable parameters. The critical property of 2-(2-EE)EA is estimated with the Joback–Lyderson method.

Experimental data up to 485 K and 206.6 MPa are reported for binary and ternary mixtures of poly(2-(2-ethoxyethoxy)ethyl acrylate) [P(2-(2-EE)EA)] + carbon dioxide + 2-(2-EE)EA, P(2-(2-EE)EA) + carbon dioxide + dimethyl ether (DME), P(2-(2-EE)EA) + carbon dioxide + propylene and P(2-(2-EE)EA) + carbon dioxide + 1-butene systems. High-pressure cloud-point data are also reported for P(2-(2-EE)EA) in supercritical carbon dioxide, propane, propylene, butane, 1-butene, and DME at temperature to 474 K and a pressure range of (8.45–206.6) MPa. Cloud-point behavior for the P(2-(2-EE)EA) + carbon dioxide + 2-(2-EE)EA system were measured in changes of the pressure–temperature (p, T) slope and with 2-(2-EE)EA mass fraction of 0.0 wt%, 5.9 wt%, 14.9 wt%, 30.3 wt% and 60.2 wt%. With 0.650 2-(2-EE)EA to the P(2-(2-EE)EA) + carbon dioxide solution, the cloud point curves take on the appearance of a typical lower critical solution temperature boundary. The P(2-(2-EE)EA) + carbon dioxide + (0.0–46.6) wt% DME systems change the (p, T) curve from upper critical solution temperature region to lower critical solution temperature region as the DME mass fraction increases. Also, the impact by propylene and 1-butene mass fraction for the P(2-(2-EE)EA) + carbon dioxide + propylene and 1-butene system is measured at temperatures to 454 K and a pressure range of (75.7 to 119.6) MPa.

1. Introduction

Over the past decades, the interest in supercritical fluid (SCF) has increased. Information on phase behavior for the polymers, monomers, and polymers + monomers in supercritical fluid solvents is of importance in related industrial processes. SCF technology has been widely applied to several industrial processes including the processing of chemical separation, pharmaceuticals, biological material, and polymer processes [1–4]. In more recent years, SCF solvents have appeared in a much more diverse array of processes such as environmentally preferable solvents for liquefaction and mixing of crystalline materials, powder formation, particle and surface impregnation, and antisolvent precipitation [5,6]. The acrylate component is widely used in modern plastic technology. The acrylate monomers and polymers are used mainly for a variety of applications such as prostheses, contact lenses, photopolymer printing plates, adhesives, and coating [7,8].

Recently, we have demonstrated that it is possible to dissolve poly(acrylate) in SCF solvents over a wide range of temperatures at high pressure if an acrylate monomer is used as cosolvent [9,10]. The cosolvent can enhance high molecular weight polymer solubility in a given solvent for several reasons. If the supercritical solvent is expanded, the addition of a dense, cosolvent reduces the density difference between the polymer and the solvent [11,12].

The primary aim of this work is to obtain the pressure-composition (p, x) isotherm data at the temperature range of (313.2 to 393.2 K) and at the pressure range of (5.11 to 22.86 MPa). The experimental data obtained in this work were correlated with the Peng–Robinson equation of state [13] (PR-EOS) using a van der Waals one-fluid mixing rule including two adjustable parameters.

The secondary aim of this work is to determine the phase behavior of poly(2-(2-ethoxyethoxy)ethyl acrylate) [P(2-(2-EE)EA)] in SCF solvents such as carbon dioxide, propane, propylene, butane, 1-butene, dimethyl ether (DME) in low molecular weight.

The cloud-point behavior for the P(2-(2-EE)EA) + carbon dioxide + 2-(2-ethoxyethoxy)ethyl acrylate [2-(2-EE)EA] and P(2-(2-EE)EA) + carbon dioxide + DME systems show the curves changing from a positive slope to a negative slope.

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The interchange that characterizes the balance of polymer segment + solvent cross interactions relative to polymer segment + polymer segment and solvent + solvent self-interactions is very sensitive to temperature due to the strong polar interactions experienced between polymer segments [14].

1.1. Experimental

1.1.1. Apparatus and procedure

The experimental apparatus and techniques used to measure the phase behavior of 2-(2-EE)EA and P(2-(2EE)EA) in supercritical carbon dioxide are described in detail elsewhere [15,16]. A variable-volume view cell used to measure the phase behavior data and operated up to pressures of 300.0 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 was moved using water pressurized by a high pressure generator (HIP, model 37-5.75-60). Pressure of the mixture was measured with a Heise gauge (carbon + monomer: Dresser Ind., model CM-53920, 0 to 34.0 MPa, accurate to within ±0.03 MPa; polymer + solvents: Dresser Ind., model CM-108952, 0 to 345.0 MPa, accurate to within ±0.35 MPa). The temperature of the cell, typically maintained to within ±0.2 K, was measured using 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 viewed 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.

At a constant temperature, the solution in the cell is maintained in the single-phase region at the desired temperature for at least 20–30 min. so that the cell can reach thermal equilibrium. The pressure is slowly decreased until the solution becomes cloudy. The cloud-point data are obtained at a constant concentration of polymer in solution. The cloud-point pressure is defined as the point at which the solution becomes so opaque that it is no longer possible to see the stir bar in the solution. Cloud-point measurements are repeated at least twice at each temperature and are typically reproducible to within ±0.8 MPa.

To determine a bubble point, a dew point and a mixture-critical point, a bubble point pressure was obtained when small vapor bubbles appeared in the cell, while a dew point was obtained after appearance of a fine mist. Mixture-critical points were obtained by adjusting the temperature and pressure of the mixture until critical opalescence was observed along with equal liquid and vapor volume upon formation of the second phase.

The solution in the cell was compressed to a single phase at a fixed temperature. The inside solution was maintained in the single phase region at the desired temperature for at least 30–40 min to allow the cell to reach phase equilibrium. The pressure was then slowly decreased until a second phase appeared.

2. Materials

Poly(2-(2-ethoxyethoxy)ethyl acrylate)[P(2-(2-EE)EA)] ($M_w = 100{,}000$; $T_g = 203.2$ K; CAS RN 27015-29-8) was obtained from Scientific Polymer Product, Inc. Upon arrival, the P(2-(2-EE)EA) was in a toluene solution, the polymer solution was placed under vacuum for at least 10 h in the Rotary Evaporator (Tamato Scientific Co., model RE-47) for removing toluene. 2-(2-Ethoxyethoxy)ethyl acrylate (2-(2-EE)EA) (mass fraction purity >0.980, CAS RN 7328-17-8) used in this work was obtained from Scientific Polymer Products, Inc. This component was used without further purification in the experiments. To prevent 2-(2-EE)EA polymerization, 2,6-di-*tert*-butyl-4-methyl phenol (Aldrich, mass fraction purity >0.990) was used as an inhibitor at a concentration of 0.005 times the amount of 2-(2-EE)EA. Carbon dioxide (mass fraction purity >0.998) was obtained from Daesung Industrial Gases Co., and propane (mass fraction purity >0.980) from LG Gas (E1), and propylene (mass fraction purity >0.996), butane(mass fraction purity >0.970), 1-butene (mass fraction purity >0.995) from Yeochun NCC Co. and dimethyl ether (DME) (mass fraction purity >0.995) from E1 Co. and used without further purification.

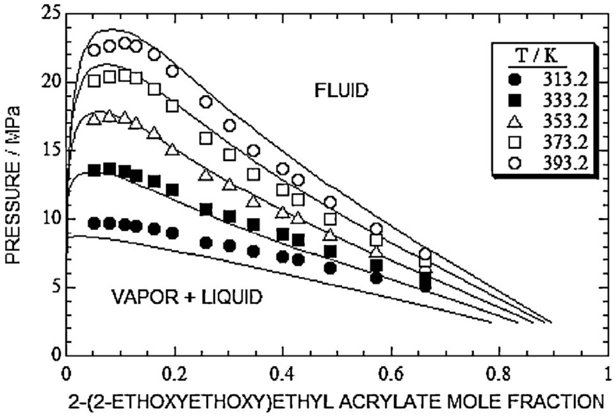

Fig. 1. Plot of pressure against mole fraction that compares the experimental data (symbols) of the (carbon dioxide + 2-(2-ethoxyethoxy)ethyl acrylate) system with calculations (solid lines) obtained with the Peng–Robinson equation of state; k_{ij} equal to 0.034 and η_{ij} equal to −0.037. ●, 313.2 K; ■, 333.2 K; △, 353.2 K; □, 373.2 K; ○, 393.2 K.

3. Experimental results and discussion

3.1. Phase behavior of CO_2 + 2-(2-ethoxyethoxy)ethyl acrylate [2-(2-EE)EA] mixture

The experimental data of bubble-point, critical-point and dew-point for binary mixtures of 2-(2-EE)EA in CO_2 were obtained, and the experimental data was reproduced at least twice to within ±0.02 MPa and ±0.2 K for a given loading of the cell. The combined standard uncertainties of pressure and temperature were estimated ±0.02 MPa and ±0.12 K. The combined standard uncertainties of 2-(2-EE)EA mole fractions are estimated to be ±0.0008 [17]. As shown in Fig. 1 and Table 1, the bubble-point, critical-point and dew-point for the CO_2 + 2-(2-EE)EA system were obtained at a temperature range from 313.2 K to 393.2 K and pressure up to 22.86 MPa.

Experimental data obtained in this study were correlated with Peng–Robinson equation of state (PR-EOS) using the van der Waals one fluid mixing rule [13] including two binary interaction parameters (k_{ij}, η_{ij}). The mixing rule in the PR-EOS is expressed as follows.

$$a_m = \sum_i \sum_j x_i x_j a_{ij} \tag{1}$$

$$a_{ij} = \sqrt{a_{ii} a_{jj}} \left(1 - k_{ij}\right) \tag{2}$$

$$b_m = \sum_i \sum_j x_i x_j b_{ij} \tag{3}$$

$$b_{ij} = \frac{b_{ii} + b_{jj}}{2} \left(1 - \eta_{ij}\right) \tag{4}$$