



Phase equilibria for the binary mixture of n-vinyl pyrrolidone and N,N-dimethylacrylamide in supercritical carbon dioxide

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ABSTRACT

High pressure phase equilibria for the (carbon dioxide + n-vinyl pyrrolidone) and (carbon dioxide + N,N-dimethylacrylamide) systems are measured in a static apparatus at five temperatures of 313.2, 333.2, 353.2, 373.2 and 393.2 K and pressures up to 24.66 MPa. These two systems exhibit maximums in pressure at temperatures between the critical temperatures of carbon dioxide and n-vinyl pyrrolidone or N,N-dimethylacrylamide. The solubility of n-vinyl pyrrolidone and N,N-dimethylacrylamide for the carbon dioxide + n-vinyl pyrrolidone and carbon dioxide + N,N-dimethylacrylamide systems increases as the temperature increases at a fixed pressure. The carbon dioxide + n-vinyl pyrrolidone and carbon dioxide + N,N-dimethylacrylamide systems exhibit type-I phase behavior. The experimental results for the carbon dioxide + n-vinyl pyrrolidone and carbon dioxide + N,N-dimethylacrylamide systems are correlated with the Peng–Robinson equation of state using a mixing rule including binary interaction parameters (k_{ij} and η_{ij}). © 2011 The Korean Society of Industrial and Engineering Chemistry. Published by Elsevier B.V. All rights reserved.

1. Introduction

The phase equilibria for binary mixture of the hydrocarbon with supercritical carbon dioxide (scCO₂) play an important role in the chemical separation process, supercritical fluid extraction, polymerization condition and industrial application [1–3]. Phase behavior experiments have recently been reported on the bubble-point, dew-point and mixture critical-point behavior of binary mixtures containing scCO₂ [4,5]. scCO₂ used in this work is widely used as an environmentally benign solvent which is inexpensive, nonflammable, and nontoxic. Also, scCO₂ has a quadrupole moment, no dipole moment, and low dielectric constant, and it is a good solvent with low molecular weight in nonpolar molecules. Therefore, phase equilibria information for binary mixture containing carbon dioxide is required for practical uses. n-Vinyl pyrrolidone monomer has the inherent properties of high polarity, low toxicity, water solubility, chemical stability and pseudo-cationic activity, and it is mainly used for a variety of applications as reactive diluents in ultraviolet and electron-beam curable polymers applied to inks, coatings or adhesives. N,N-Dimethylacrylamide is used for coating agents, fiber and plastic amelioration, fibers and papers treatment, photographs and printing material, cosmetics/pharmaceuticals and other applications [6]. The information on the high pressure behavior for the n-

vinyl pyrrolidone and N,N-dimethylacrylamide in supercritical carbon dioxide has been valuable in the design of new separation processes and optimum condition of polymerization.

Phase behavior data for the carbon dioxide + n-vinyl pyrrolidone and carbon dioxide + N,N-dimethylacrylamide systems were reported by Bae et al. [7] and Santos et al. [8]. Bae et al. used a static apparatus and presented the liquid–vapor equilibrium curves for carbon dioxide + n-vinyl pyrrolidone mixture at temperatures from 324 K to 355 K and pressures up to 19.00 MPa. Santos et al. reported the phase equilibrium data for the carbon dioxide + N,N-dimethylacrylamide system at a temperature range from 303.15 K to 358.15 K and pressure up to 16.52 MPa. Byun et al. [9] reported the phase behavior curves for the carbon dioxide + amides systems at temperatures from 318.2 K to 398.2 K and pressures up to 25.00 MPa using a static apparatus.

In this work, the measurement is aimed at obtaining the phase equilibrium data for carbon dioxide + n-vinyl pyrrolidone and carbon dioxide + N,N-dimethylacrylamide mixtures by investigating mixtures of carbon dioxide with two components using a variable volume view cell at temperature from 313.2 K to 393.2 K and pressure up to 21.60 MPa. Also, the pressure–temperature (P – T) diagrams of the mixture critical curve are presented for the carbon dioxide + n-vinyl pyrrolidone and carbon dioxide + N,N-dimethylacrylamide systems in the vicinity of the critical point of pure carbon dioxide. The experimental data for carbon dioxide + n-vinyl pyrrolidone and carbon dioxide + N,N-dimethylacrylamide systems obtained in this work are correlated with the Peng–Robinson equation of state [10] using a van der Waals one-fluid

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mixing rule including two adjustable parameters. The properties of critical pressure, critical temperature, and acentric factor of *n*-vinyl pyrrolidone and *N,N*-dimethylacrylamide are reported in the literature and calculated [7,11], while the vapor pressure is estimated by the Lee–Kesler method [11].

2. Experimental

2.1. Apparatus and procedure

Described in detail elsewhere are the experimental apparatus and techniques used to measure the phase equilibria of monomers in *scCO*₂ [12,13]. The main components of experimental apparatus are high-pressure generator, variable volume view cell (in air bath), and visual apparatus. A high pressure generator (HIP, model 37-5.75-60) was pressurized with the movement of the piston (2.54 cm length) by using water. The pressure in view cell is measured with a Heise gauge (Dresser Ind., model CM-53920, 0–34.00 MPa) uncertainty to ±0.02 MPa. The variable volume view cell (6.4 cm outer diameter × 1.59 cm inside diameter, a working volume of ~28 cm³) operating a high pressure is used to obtain the bubble-point, dew-point and mixture critical-point curves, and is capable of operating to pressure of 70.00 MPa. Magnetic stirring bar in the view cell ensures mixing solution rapidly reaching equilibrium. A sapphire window (1.2 cm thick × 1.9 cm diameter) is fitted in the front part of the cell to allow observation of the phases. The visual parts are borescope, monitor (M&J Technology Co., model HT-1900WT) and flexible light guide. 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. Also, a flexible light guide connected between a high density illuminator (Dolan-Jenner Industries Inc., model PL-800) and the borescope is used to transmit light into the view cell.

First, the empty view cell is purged several times with carbon dioxide and nitrogen to remove traces of air and organic matter. Typically, *scCO*₂ is added to the cell using a high pressure bomb, uncertainty to within ±0.002 g. The monomer is loaded into the cell using a syringe, uncertainty to within ±0.001 g. The mixture in the cell is compressed to the desired pressure (single phase) by moving a piston located within the cell. The inside solution is maintained in the single phase (fluid) region at the desired temperature for at least 30–40 min for the cell to reach phase equilibrium. The pressure is then slowly decreased until a second phase appears. A bubble point pressure is obtained when small vapor bubbles appear first in the cell, while a dew point is obtained if fine mist appears in the cell. Critical points are obtained by adjusting the temperature and pressure of the mixture until critical opalescence is observed along with equal liquid and vapor volumes upon the formation of the second phase.

2.2. Materials

Carbon dioxide (mass fraction purity > 0.998) is obtained from Daesung Industrial Gases Co. (Yeosu, Korea) and used as received. The *n*-vinyl pyrrolidone (mass fraction purity ≥ 0.990, CAS RN 88-12-0) and *N,N*-dimethylacrylamide (mass fraction purity: 0.990, CAS RN 2680-03-7) used in this work are obtained from Sigma-Aldrich Co. Two components are used without further purification in the experiments.

3. Experimental results and discussion

High pressure phase equilibria data for the *n*-vinyl pyrrolidone and *N,N*-dimethylacrylamide in carbon dioxide are measured and reproduced at least twice, uncertainty to within ±0.02 MPa and ±0.2 K for a given loading of the cell. The mole fractions are uncertainty to within ±0.002.

Fig. 1 is the result of the phase equilibrium experiment conducted on carbon dioxide + *n*-vinyl pyrrolidone (above) system at 333.2 K and 353.2 K and carbon dioxide + *N,N*-dimethylacrylamide system at 313.2 K and 333.2 K in order to verify our apparatus. As shown in Fig. 1, the result shows good agreement between the experimental results and the ones reported by Bae et al. [7] at 335.1 K and 355.8 K (above). Also, the comparison result for the carbon dioxide + *N,N*-dimethylacrylamide system shows slightly pressure difference between the experimental results and the ones reported by Santos et al. [8] at 313.2 K and 333.2 K.

Fig. 2, Tables 1 and 2 show the pressure–composition (*P*–*x*) isotherms at *T* = 313.2, 333.2, 353.2, 373.2 and 393.2 K, and pressures from 3.10 to 24.66 MPa for the carbon dioxide + *n*-vinyl pyrrolidone and carbon dioxide + *N,N*-dimethylacrylamide systems. Both the systems do not exhibit three phases at five temperatures investigated. As shown in Fig. 2, the mixture critical pressure was observed around 24.66 MPa at 393.2 K for the carbon dioxide + *n*-vinyl pyrrolidone system, and around 15.79 MPa at 353.2 K and around 21.62 MPa at 393.2 K for the carbon dioxide + *N,N*-dimethylacrylamide system. The critical curves for the carbon dioxide + *n*-vinyl pyrrolidone and carbon dioxide + *N,N*-dimethylacrylamide mixtures exhibit maximum pressures in *P*–*T* space.

The experimental data were correlated with the Peng–Robinson equation of state (EOS) using van der Waals one fluid mixing rule including two parameters. The Peng–Robinson EOS [10] is used with the following:

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

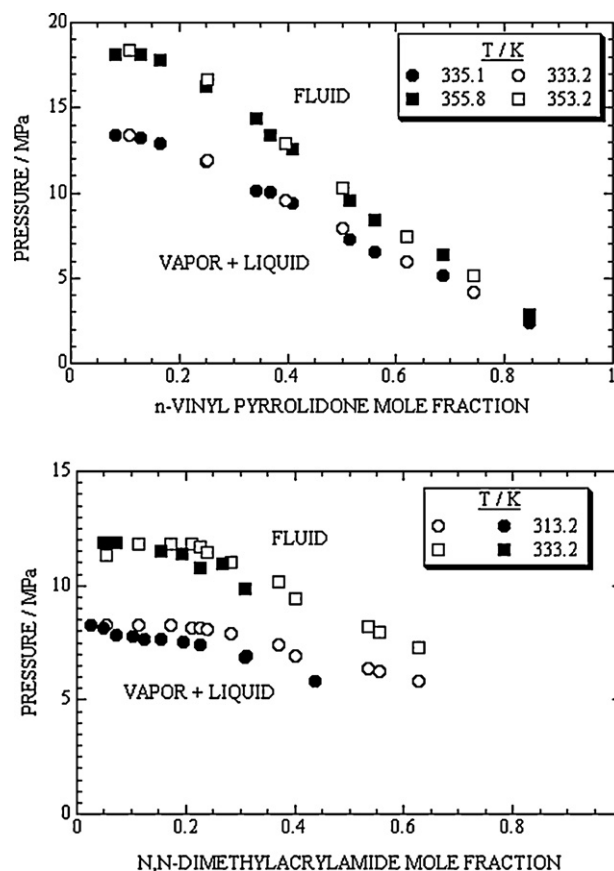


Fig. 1. Phase equilibrium compared between the experimental data (○: 333.2 K and □: 353.2 K) and reported data by Bae et al. (●: 335.1 K and ■: 355.8 K) for the carbon dioxide + *n*-vinyl pyrrolidone (above) system, and between the experimental data (○: 313.2 K and □: 333.2 K) and reported data by Santos et al. (●: 313.2 K and ■: 333.2 K) for the carbon dioxide + *N,N*-dimethylacrylamide (bottom) system.

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