



# Phase equilibrium of PVAc + CO<sub>2</sub> binary systems and PVAc + CO<sub>2</sub> + ethanol ternary systems

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## ARTICLE INFO

### Article history:

Received 17 August 2017

Received in revised form

10 November 2017

Accepted 20 November 2017

Available online 26 November 2017

### Keywords:

Phase equilibrium

Poly(vinyl acetate)

CO<sub>2</sub>

Ethanol

PC-SAFT

## ABSTRACT

The cloud point and bubble point isopleths were measured for poly(vinyl acetate) (PVAc) + CO<sub>2</sub> binary systems and PVAc + CO<sub>2</sub> + ethanol ternary systems using a supercritical CO<sub>2</sub> phase equilibrium apparatus. A transition point measurement device was designed to accurately determine the cloud point pressures by measuring the resistance variation of a photoresistor. The effects of the temperature, pressure, components, and polymer molecular weight on the phase behavior of these binary and ternary systems were investigated. We found that the transition point pressure increased with increasing temperature and molecular weight of PVAc, the cloud point isopleths for the PVAc + CO<sub>2</sub> binary systems are upper critical solution pressure (UCSP) type, the cloud point pressures moved downwards with the addition of ethanol to PVAc + CO<sub>2</sub>, and the cloud point pressures decreased with increasing PVAc + ethanol concentration at a fixed mass ratio of 1:7. The perturbed-chain statistical associating fluid theory equation of state (PC-SAFT EOS) was used to investigate the phase behavior of these binary and ternary systems by adjusting the binary interaction parameter,  $k_{ij}$ . The modeling shows a very good agreement with the experimental data.

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## 1. Introduction

CO<sub>2</sub> is increasingly valued in unconventional oil and gas development as a drilling fluid, fracturing fluid, and oil displacement agent instead of water because of the specific geological conditions of oil reservoirs and the need for environmental protection [1]. However, the application of CO<sub>2</sub> in petroleum engineering is limited because of the low viscosity and density of supercritical CO<sub>2</sub>. CO<sub>2</sub> can reduce the carrying capacity of the drilling fluid and fracture fluid and decrease the sweep efficiency in enhanced oil recovery because of its low viscosity and density [2]. Therefore, it is necessary to increase the viscosity and density of CO<sub>2</sub> by adding a polymer and cosolvents at moderate temperatures ranging from about 300 to 350 K and pressures up to about 50 MPa for the oil and gas development process [3,4].

As a weak solvent that can form weak complexes with basic

functional groups in polymers [5], CO<sub>2</sub> is unable to dissolve most polymers under moderate conditions (273–373 K, 0–50 MPa), in addition to amorphous fluoropolymers [6] and polysiloxanes [7]. However, homopolymers with hydrocarbon and oxygen-containing groups alone, such as poly(vinyl acetate) (PVAc), have been shown to be reasonably soluble in CO<sub>2</sub> because of the amorphous structure and low melting point and weak Lewis acid–base interactions between the acetate group and CO<sub>2</sub> [8]. However, relatively low molecular weight PVAc can be dissolved in CO<sub>2</sub> above 30 MPa [9,10]. Therefore, some cosolvents must be added to the (polymer + CO<sub>2</sub>) system to shift the transition point curve to relatively low temperatures and pressures [11,12].

A cosolvent can greatly decrease the transition point pressure of the (polymer + CO<sub>2</sub>) system for several reasons. The cosolvent can reduce the free volume difference between the polymer and CO<sub>2</sub> [13]. In addition, it can provide favorable physicochemical interactions to increase the region of miscibility [14]. Previous works have shown many phase behaviors in (polymer + CO<sub>2</sub> + cosolvent) systems [15]. Polar cosolvents are often added to increase the solubility of polymers in CO<sub>2</sub> [5], as long as the cosolvent does not form a complex with the polar repeat units in the polymer [16]. The

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polar cosolvents in ternary systems are often the monomer of the polymer or an organic solvent that has a similar structural formula to the monomer, such as methyl methacrylate (MMA) in poly(methyl methacrylate) (PMMA) [17], ethanol in poly(ethylene glycol) (PEG) [18], ethylene in poly(ethylene-co-vinyl acetate) (PEVA) [19], and dodecyl methacrylate (DDMA) or dimethyl ether (DME) in poly(dodecyl methacrylate) (PDDMA) [20]. Using a CO<sub>2</sub>-philic homopolymer, experimental data for the binary system (PVAc + CO<sub>2</sub>) has been reported many times [8,21–23], but reports on the modeling of this binary system are scarce. Meanwhile, there have been few reports concerning the influence of the cosolvent on the solubility of PVAc in CO<sub>2</sub> [15].

In this work, a photoresistor transition point measurement device was designed to significantly reduce the error caused by visual observation. Three different molecular weights of PVAc were selected and used. The phase equilibrium of poly(vinyl acetate) + CO<sub>2</sub> binary systems were determined under moderate temperatures ranging from 308.2 to 338.2 K and at pressures of up to 50 MPa. The effects of the temperature, mass fraction, and molecular weight of PVAc on the phase transition pressure were discussed. In addition, ethanol was chosen as the cosolvent because it is an appropriate cosolvent for supercritical CO<sub>2</sub> and is more environmentally friendly than many organic solvents. The PVAc + CO<sub>2</sub> + ethanol ternary systems were investigated under the same conditions as the binary systems described above. Finally, the perturbed-chain statistical associating fluid theory equation of state (PC-SAFT EOS) was used to correlate the experimental data because it is widely applicable to many polymer + CO<sub>2</sub> and polymer + CO<sub>2</sub> + cosolvent systems [15].

## 2. Experimental

### 2.1. Materials

CO<sub>2</sub> was obtained from Qingdao Tianyuan Industrial Gas Co., Ltd, with a mass fraction of more than 99.99%. Ethanol with a mass purity of more than 99.5% was obtained from Guangdong Xilong Chemical Co., Ltd. Three different molecular weights of PVAc were supplied by Sigma-Aldrich Co., Ltd. The molecular weight distributions of the PVAc samples were determined by gel permeation chromatography (GPC) [24] and are shown in Fig. 1. All the materials used were tabulated in Tables 1 and 2. All reagents were used

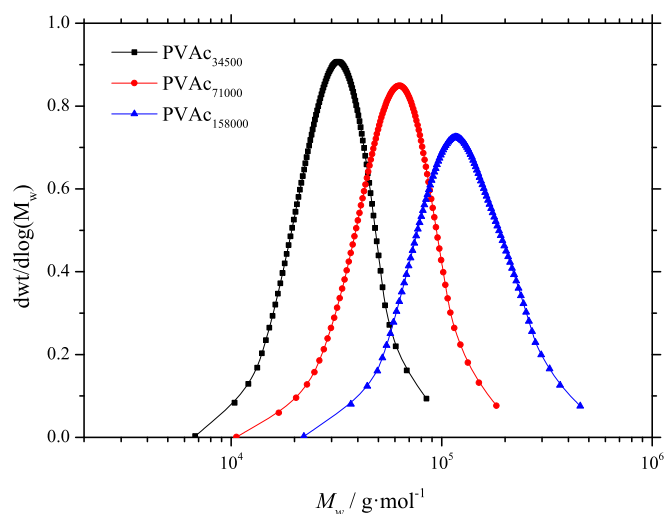


Fig. 1. GPC distribution of the PVAc samples. The ordinate indicates the derivative of the mass fraction ratio to the logarithm of  $M_w$ .

without further purification.

### 2.2. Apparatus and procedure

The cloud point and bubble point pressures of PVAc in the binary or ternary system were measured using a supercritical CO<sub>2</sub> phase equilibrium apparatus. A schematic diagram of this apparatus is shown in Fig. 2.

The apparatus included a view cell component, a supercharging system, and a cloud-point measurement device. Two sapphire windows were fixed on both sides of the view cell to enable the penetration of light. The volume of the view cell was variable between 150 and 350 mL by utilizing a servomotor to control the piston movement. The pressure of the view cell could be measured with a pressure sensor connected to a programmable logic controller (PLC), which could adjust pressure utilizing a servomotor to control the piston movement. A magnetic-coupled drive was fixed under the view cell to adjust the stirring speed to between 0 and 1000 rpm. The temperature of the view cell was measured with a temperature sensor connected to an oil bath heating jacket, which was an interlayer surrounding the view cell. The maximum temperature of the view cell components was 423 K, and the maximum pressure was 50 MPa. The uncertainty for temperature measurement was  $\pm 0.01$  K and that for pressure was  $\pm 0.01$  MPa.

In a typical experiment [17], a known amount of PVAc and ethanol were added into the view cell, and then the view cell was purged with nitrogen several times using a vacuum pump. The uncertainty for mass measurement of PVAc and ethanol was  $\pm 0.001$  g. After that, the storage tank was pressurized with CO<sub>2</sub> from a cylinder utilizing the supercharging system that included a plunger pump, an intermediate container, and a water pool. After the pressure in the storage tank had reached 50 MPa, the globe valve was opened so the high-pressure CO<sub>2</sub> could flow into the view cell. The amount of CO<sub>2</sub> in the view cell was measured with a balance. The uncertainty for mass measurement of CO<sub>2</sub> was  $\pm 0.1$  g. The transition point measurement device was installed after all the CO<sub>2</sub> had been injected into the view cell. A parallel light source was fixed on one side of the sapphire window, while a photoresistor connected to a multimeter was fixed on the other side. Then, the stirring speed and temperature were set at fixed values and the pressure was set to 50 MPa to form a transparent and homogeneous binary or ternary system. Meanwhile, the resistance of the photoresistor was measured. Afterward, the pressure was decreased at a rate of about  $\Delta p = 0.5$  MPa min<sup>-1</sup> until the polymer-rich phase or polymer-lean phase separated from the mixture. In this process, the resistance shown on the multimeter increased rapidly until it was out of range. Then, the pressure was increased at the same rate until the mixture became a transparent, homogeneous system again and the resistance returned to its previous value. The phase transition point was taken as the derivative extremum of the resistance–pressure curves (shown in Fig. 3). The liquid–liquid equilibrium (LLE) or vapor–liquid equilibrium (VLE) could be distinguished by visual observation. The experiments were repeated at least three times.

Fig. 3 shows an example of the determination of the transition. The resistance–pressure curve of the PVAc<sub>34500</sub> (1) + CO<sub>2</sub> (2) + ethanol (3) system with mass fractions of  $w_1 = 0.030$ ,  $w_2 = 0.760$ , and  $w_3 = 0.210$  at 308.15 K was measured. The curve plateaued when the pressure decreased from 20 to 14 MPa. Then, the resistance showed a sharp rise with a relatively small decrease in differential pressure. The derivative of this curve marks the cloud point pressure accurately. The cloud point pressure of this system is 13.87 MPa, which was determined from the extremum of  $dR/dp$ . All cloud-point experiments and bubble-point pressures were determined by this method, which can reduce the error caused by visual

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