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Experimental measurements and thermodynamic modeling of the cloud point pressure for solubility of copolymers of vinyl acetate and dibutyl maleate in supercritical CO_2

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ABSTRACT

In this study the cloud point pressure for the solubility of copolymers of vinyl acetate and dibutyl maleate in supercritical carbon dioxide were measured and modeled. The copolymers investigated have different molecular weights, with varying structures. The cloud point pressure data were modeled using the Perturbed Chain Polar Statistical Associating Fluid Theory (PCP-SAFT) equation of state (EoS) that was developed for the prediction of the phase behavior of polar polymers which are soluble in supercritical carbon dioxide (J. of Supercritical Fluids 97 (2015) 45–50). Using this model, the cloud point pressure of the polymer-supercritical CO_2 systems were correlated by taking into account quadrupole-quadrupole interactions between carbon dioxide and the polymer segments through the PCP-SAFT EoS. Thus, the new parameters were determined for the copolymers studied in this work. Moreover, we applied PC-SAFT EoS for the same systems. It is shown that the results are obtained using the PCP-SAFT EoS is superior respect to PC-SAFT so that the present EoS can be applied to calculate the cloud point pressure of the copolymer-CO_2 systems and the deviation of the calculated values from experiment values are low.

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1. Introduction

Supercritical fluids have been extensively investigated by scientists and engineers over the last few decades due to their wide range of applications in the oil, gas and chemical and petrochemical industries. Among the supercritical fluids, carbon dioxide can be considered the most important and has been extensively used in many physical and chemical processes, such as separation, extraction, polymerization, etc. CO_2 is a clean and versatile fluid which has moderate critical conditions and has several suitable specifications, being nonhazardous, nonflammable, relatively cheap, and abundantly available. Carbon dioxide has been used in a variety of polymeric processes such as polymerization, plasticization, polymer fractionation, coating and lithography [1]. Moreover using ultrasound, carbon dioxide in conjunction with water can produce a biphasic system that is environmentally benign and nontoxic. These supercritical CO_2–water mixtures are applied in a variety of chemical reactions through the making of emulsions and microemulsions [2]. Recently, supercritical carbon dioxide has been used in the semiconductor industry in a novel electroplating technique that is not only environmentally friendly, but also presents various advantages in comparison to the traditional methods [3]. In the pharmaceutical and food industries, pressurized carbon dioxide has been used for the sterilization of microorganisms such as bacteria, filamentous fungi, and yeasts. In this application, carbon dioxide which has a moderate critical state is used to sterilize thermal-sensitive materials, such as vegetables at non-thermal conditions [4].

From an environmental perspective, carbon dioxide has been promoted as a green solvent that is a good alternative to organic

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solvents, especially in polymerization processes [1]. However, a limited number of groups of polymers are soluble at carbon dioxide, such as fluoro polymers and polymers based on siloxane and vinyl acetate [5]. Among these polymers, poly(vinyl acetate) has drawn the most attention because of its low cost and being considered environmentally more attractive.

Carbon dioxide is a good choice for enhanced oil recovery (EOR) through gas injection [5,6]; however, it presents two significant disadvantages, viz. low viscosity at the reservoir conditions, and its permeability in the production wells, rather than displacing the oil ahead of it. In order to resolve these drawbacks, polymers can be dissolved in supercritical CO_2 to enhance its viscosity and reduce its diffusivity. The solubility of polymers in supercritical carbon dioxide fluid can be measured through the determination of the cloud point pressure at a fixed temperature, concentration, and at high pressure using a variable-volume transparent cell [5].

In previous studies, researchers have focused on the synthesis of soluble polymers in supercritical carbon dioxide fluid; however there are few proper models which represent the phase behavior of the polymer-supercritical CO_2 systems in terms of correlation and prediction of the cloud point pressure of such systems. Byun and McHugh measured the cloud point pressure of poly(isopropyl acrylate) in supercritical solvents such as CO_2, propane, propylene, butane, 1-butene, and dimethyl ether. Using two temperature-independent interaction parameters, they applied the Peng-Robinson EoS successfully for thermodynamic modeling of these systems [7]. Kasturirangan and Teja modeled the CO_2 + biopolymer and CO_2 + fluoropolymer systems using the modified gART-L model [8] that was extended for modeling the three component systems of Yuan and Teja [9]. They used two temperature-dependent interaction parameters, one of which was obtained using FTIR spectroscopy. Stoychev et al. used the PC-SAFT EoS to model the cloud point pressure of two types of poly(propylene oxide) and six types of poly(ethylene oxide)-b-poly(propylene oxide)-b-poly(ethylene oxide) in supercritical carbon dioxide fluid. They showed that the equation of state was successful in the prediction of the phase behavior of these polymer-CO_2 systems using a single temperature-independent interaction parameter [10]. Schacht et al. proposed the PCP-SAFT EoS for modeling the phase behavior of the hyper branched polyglycerol-methanol-CO_2 system [11]. This EoS was successful in vapor-liquid, liquid-liquid, and vapor-liquid-liquid equilibrium computations, as well as the bubble point and cloud point pressure calculations.

In our previous work, a model was developed to correlate the cloud point pressure of several copolymer- supercritical CO_2 systems using the PCP-SAFT equation of state [6]. The interaction between polymer segments and CO_2 was considered as quadupole-quadrupole to enable the phase behavior of the polymer- supercritical carbon dioxide systems to be correlated accurately. Moreover, a correction to a term for the chemical potential of the hard-chain in the original PC-SAFT article was made [6,12]. In this work, new experimental data for the cloud point pressure were obtained using a variable-volume high pressure viewing cell. The experimental data were correlated with the PCP-SAFT EoS.

2. Experimental

2.1. Materials

Carbon dioxide (99.9%) was purchased from Afrox South Africa. The copolymers, structures presented in Figs. 1–2, were synthesized by the polymer group in the Department of Chemical Engineering at Tarbiat Modares University [13,14]. The specifications of the copolymers investigated in this study are shown in Table 1, where type C1 is an alternative copolymer and the others are random copolymer. As shown in Fig. 2, the variables x and y denote the monomer fractions of vinyl acetate and dibutyl maleate in the polymer chain, respectively. For validation of the measurement data, a commercially available poly(dimethyl siloxane), purchased from Gute Chemie, was used.

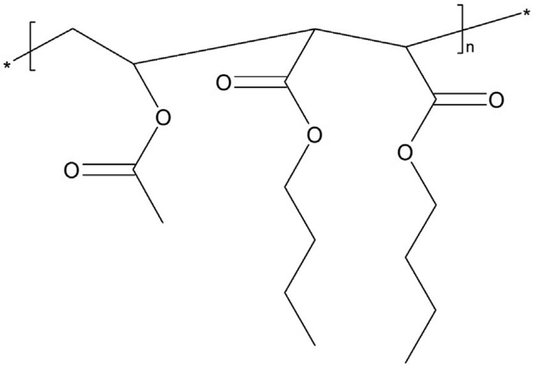

Fig. 1. The structure of alternative poly(vinyl acetate-alt-dibutyl maleate).

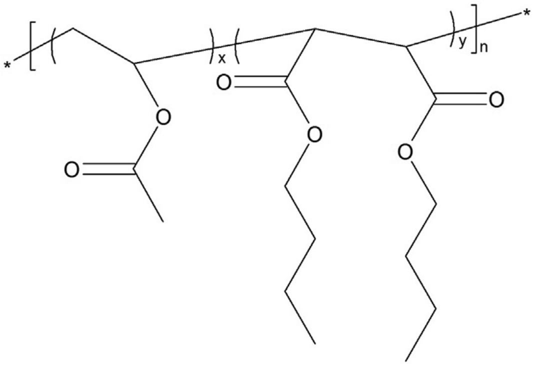

Fig. 2. The structure of random copolymer containing vinyl acetate (x) and dibutyl maleate (y).

2.2. Purification of the polymers using CO_2

A typical purification process begins with a given polymer being introduced into the cell. The cell is evacuated to a very low pressure. Thereafter, supercritical carbon dioxide is fed into the cell using a piston pump and the mixture of supercritical CO_2 and polymer is stirred vigorously under a pressure of approximately 100 bar at ambient temperature for a period of 1 h. The majority of the carbon dioxide is thereafter purged and fresh carbon dioxide introduced into the cell. The mixture is again stirred under pressure of approximately 50 bar at equilibrium conditions for 1 h. The carbon dioxide is then completely purged and a purified polymer is obtained.

2.3. The apparatus

The phase behavior investigations were undertaken on a high pressure variable-volume transparent cell. The cell used in this study is a modification of the one described in a previous study [15]. The major modification was to the flanges which enabled a larger operating pressure range. The cell comprises of a cylindrical sapphire tube, purchased from Rayotek Scientific, which is contained between two SS 316L metal flanges which were compressed and sealed using O-rings. The dimensions of the tubular cell are 70 mm

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