PHASE BEHAVIOR OF THE TERNARY SYSTEM POLY (ε-CAPROLACTONE) - CARBON DIOXIDE - DICHLOROMETHANE

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Abstract: This works investigates the phase behavior of poly(ε-caprolactone) in mixtures of carbon dioxide with dichloromethane in the temperature range from 303.15 to 343.15 K, pressures up to 210 bar over a wide overall compositional range. The experimental data were measured using a variable-volume view cell adopting the static synthetic method. A polymer of low-molecular weight (M_w=10 000) was used at mass fractions of 0.01, 0.03, 0.05 and 0.07. For these systems, vapor- liquid (VL), liquid-liquid (LL) and three-phase vapor-liquid-liquid (VLL) equilibrium were observed in the experimental range of variables investigated.

Introduction

Over recent decades, considerable research effort has been directed to produce micro and nanoparticles of biodegradable polymers and polymeric particle coatings with wide applications in various important industries such as pharmaceutical, food, agrochemical, cosmetics and biomedical[1-4]. A promising approach to produce biodegradable polymers, which was originated in the 80's and received with much enthusiasm by the ''green'' movement, was the development of polymeric materials from non-toxic precursors that can fully degrade in the natural environment.

A considerable research is currently in progress aiming at the development of such biodegradable materials with emphasis on the control of final material properties[5]. One polymeric material that emerged from this effort were the caprolactone copolymers, due to the attractive characteristics of these aliphatic polyesters for biomedical, pharmaceutical controlled release systems, and other medical applications, like suture filaments, because of their biodegradability, biocompatibility and non-toxicity to the human body[6-8].

There are some articles in the literature reporting the mechanism of caprolactone polymerization and particle encapsulation with polymers in supercritical carbon dioxide[8-11] as an alternative to replace the conventional process of polymeric particle coating, as it usually involves the use of large amount of organic solvents thus arising serious air and water pollution concerns. Recently, Howdle et al.[11] reported the kinetics of enzymatic ring-opening polymerization of ε-caprolactone in supercritical carbon dioxide using *Candida antarctica* lipase B as catalyst, and results showed that high molecular weight polymers could be obtained.

With respect to industrial process, the technology of pressurized fluids emerges as an economically viable alternative and ecologically correct in various processes. The use of supercritical carbon dioxide as a medium for polymer synthesis and for polymer processing comprises interrelated research areas, which have attracted much attention recently. There are a number of well-known factors that make carbon dioxide a desirable solvent for carrying out polymerization reactions. From an industrial perspective, CO_2 is inexpensive, non-toxic, non-flammable, and readily available in high purity from a variety of sources. From a chemical perspective, CO_2 is relatively inert. This has allowed the synthesis of polymers by a wide variety of mechanisms, including free-radical chain growth, cationic chain growth, oxidative coupling, transition metal catalysis, and melt phase condensation polymerization[12].

However, due to interest in the of polymerization reactions, production of micro and nanoparticles, polymeric particle coating, impregnation of active compounds in polymeric films, the knowledge of phase behavior involving biodegradable polymer and supercritical fluids mixtures is needed in

developing new industrial applications. Also, when producing the polymer particles it is important to kwon the location of the phase boundary for the monomers-solvent systems and polymer-solvent systems. Recently, supercritical CO_2 has been investigated as a viable solvent for processing biodegradable monomers[13] and polymers of lactones[14]. For example, Kalogiannis and Panayiotou[14] investigated the bubble and cloud points of systems formed by poly(ε-caprolactone) + carbon dioxide + dichloromethane or chloroform and demonstrated the importance of the knowledge of phase behavior for polymerization reaction purposes. The poly(ε-caprolactone) used by these authors had a molecular weight of 122400, while the present data refer to a polymer of molecular weight of 10000 In this context, this work investigates the phase behavior of the ternary system poly (ε-caprolactone) - carbon dioxide – dichloromethane.

Experimental

Materials

Poly(ε-caprolactone) (PCL) (M_w = 10000; polydispersity index, I = 1.4) was purchased from Sigma-Aldrich and used without any additional treatment. The carbon dioxide (purity 99.5%) was supplied by White Martins S.A. and dichloromethane (DCM) (purity 99.5%) was purchased from Merck.

Apparatus and Experimental Procedure

Phase equilibrium experiments were conducted employing the static synthetic method in a high-pressure variable-volume view cell. The experimental apparatus and procedure have been used in a variety of studies[15,16]. Briefly, the experimental set-up consists of a variable-volume view cell with two sapphire windows for visual observation, an absolute pressure transducer (Smar LD 301), with a precision of ±0.03 MPa, a portable programmer (Smar, HT 201) for the pressure data acquisition and a syringe pump (ISCO 260D). The equilibrium cell contains a movable piston, which permits the pressure control inside the cell. Phase transitions were recorded visually through manipulation of the pressure using the syringe pump and the solvent as pneumatic fluid.

Initially, a precise amount of the polymer was and organic solvent were weighed on a precision scale balance (Gilbertini E254 with 0.0001g accuracy) and loaded into the equilibrium cell. The cell was then flushed with low-pressure CO_2 to remove any residual air. The charge of a known amount of CO_2 was performed with the help of the syringe pump (resulting accuracy of ± 0.005g in CO_2 loadings). Based on the uncertainty in CO_2 loading and other compounds weighing, we estimate that the uncertainty in global concentrations of the mixtures is lower than 0.005% in weight basis. Then, the cell content was kept at continuous agitation with the help of a magnetic stirrer and a teflon-coated stirring bar. The temperature control was then turned on, and once the desired temperature was reached, controlled within 0.5K, the pressure system was increased until the visualization of a one-phase system in the cell. At this point the system was kept at least 30 min to allow stabilization, and then the pressure was slowly decreased (typically at a rate of 1.0-3.0 bar/min) until incipient formation of a new phase. This procedure was repeated at least three times for each temperature and global composition.

Results and Discussion

In order to study the ternary system formed by PCL + dichloromethane + carbon dioxide the different PCL compositions were investigated for temperature ranging from 303.15 to 343.15 K and pressures up to 200 bar. Following the procedure described previously, we obtained the experimental data for the cloud and bubble points (BP) of the ternary system.

Figures 1 to 4 present pressure-temperature diagrams for 0.01, 0.03, 0.05 and 0.07 mass fractions of PCL, respectively. Each curve corresponds to a specific CO_2/DCM ratio. In the low temperature region a L-V transition occurs, leading to the formation of a bubble in the mixture during depressurization. However, as the temperature increases, a corresponding increase in the pressure

where the L-V occurs is noted. Beyond a certain temperature, the L-V transition is replaced by a L-L transition, which is characterized by the formation of a cloud.

The temperature region where the shift from the L-V to the L-L transition occurs depends on the PCL mass fraction and the CO_2/DCM loadings. In L-L transitions the temperature increase has a significant positive effect on the cloud point, i.e., also increases with increasing temperature. Due to its polarity, dichloromethane is a good solvent for PCL, whereas CO_2 is not. Hence, a decrease in dichloromethane composition causes a corresponding decrease in solvent mixture polarity and thus, the solvent power of the mixture is decreased, which shifts pressure transition of one-phase region towards higher values.
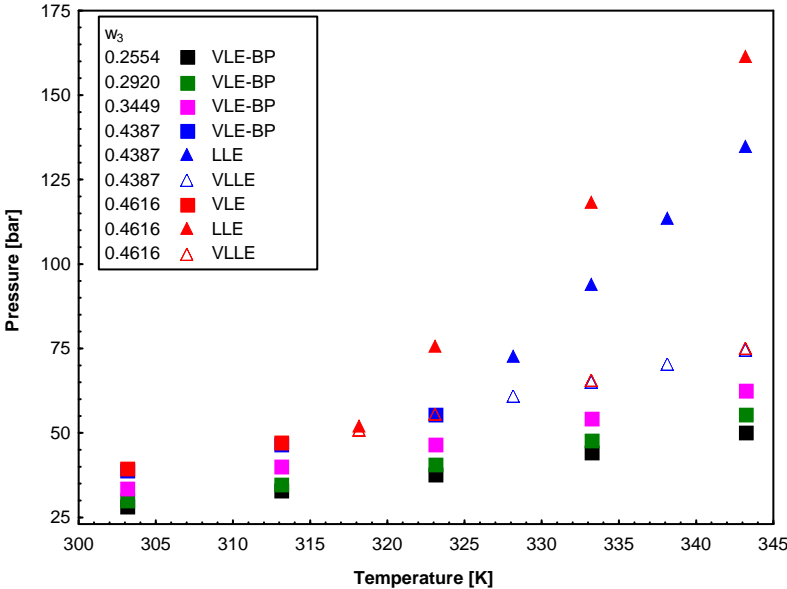

Figure 1. P-T isopleths of bubble and cloud points for the ternary system PCL (1) + DCM(2) + CO_2(3). Mass fraction of PCL = 1 wt% in DCM + CO_2.
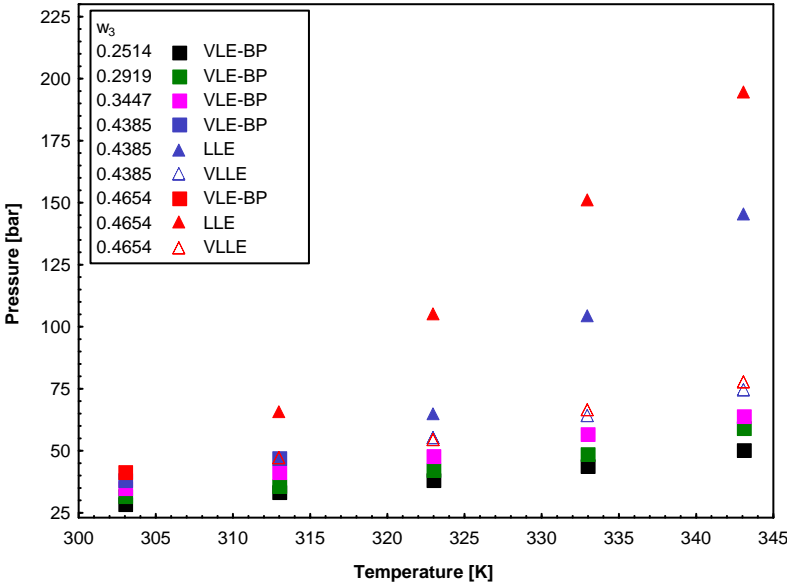

Figure 2. P-T isopleths of bubble and cloud points for the ternary system PCL (1) + DCM(2) + CO_2(3). Mass fraction of PCL = 3 wt% in DCM + CO_2.
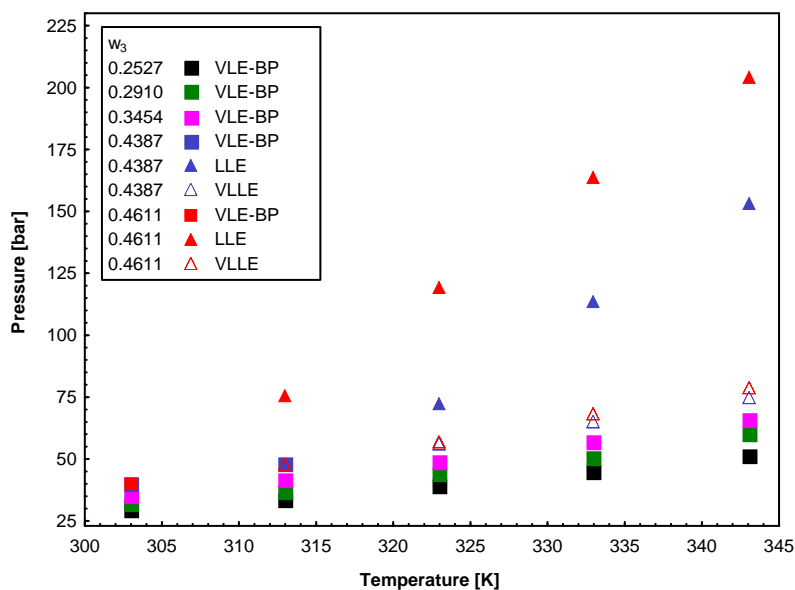
Figure 3. P-T isopleths of bubble and cloud points for the ternary system PCL (1) + DCM(2) + CO_2(3). Mass fraction of PCL = 5% in DCM + CO_2.
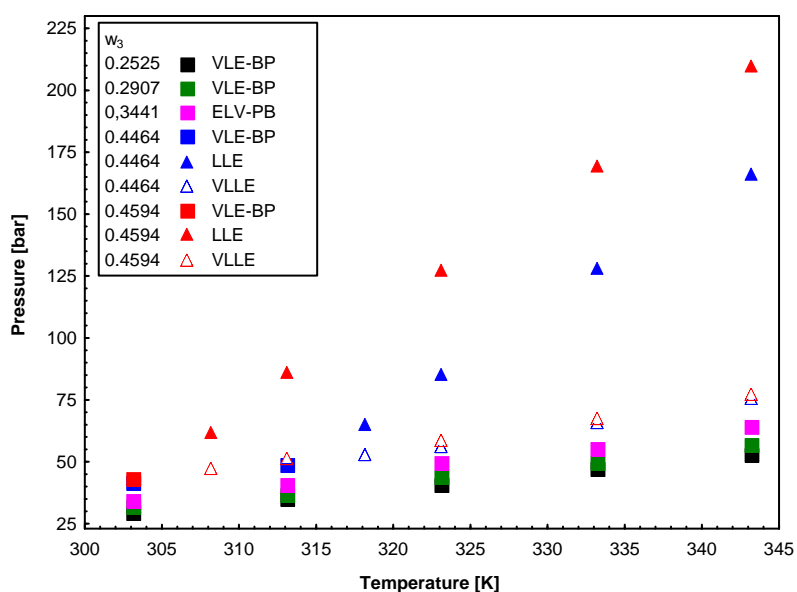

Figure 4. P-T isopleths of bubble and cloud points for the ternary system PCL (1) + DCM(2) + CO_2(3). Mass fraction of PCL = 7% in DCM + CO_2.

As shown in Figures 1 to 4, the L-L transition is shifted to lower temperatures with increasing amounts of CO_2, a fact allowing for the manipulation of the system conditions in a way that is beneficial to the particle production process. Carbon dioxide acts as an antisolvent in this system, lowering the temperature where the cloud point is first observed for a given composition of the system. Figures 1 to 4 show that all systems exhibit the *Lower Critical Solution Temperature* (LCST) behavior, which means that an increase in temperature and CO_2/organic solvent results in an enhancement in the necessary pressure to reach the one-phase region.

Another important factor that must be taken into consideration in the case of ternary mixtures is the polymer mass fraction. An increase of the mass fraction from 1 wt% to 3 wt% leads to an elevation of the cloud point around 10 bar, depending on the CO_2 mass fraction of the mixture. CO_2-rich mixtures are more influenced since they are not strong solvents of the polymer, thus an increase of CO_2 mass fraction results in higher pressure transition values.

During the L-L transition, two liquid phases appear, one rich in carbon dioxide (thus, poor in polymer), and the other, rich in organic solvent (thus, rich in polymer). In a system exhibiting LCST behavior, an increase in carbon dioxide or temperature results in the expansion of the system. In simple words, the polymer antisolvent, in the present case carbon dioxide, tends to swell and dissolve the organic solvent, reducing its solvent strength. As a consequence, higher pressures are necessary to maintain the mixture in a single phase. In the case of a strong organic solvent, the increase in the polymer mass fraction has a less pronounced effect since a smaller amount of organic solvent is needed for the dissolution of the polymer in the liquid phase rich in organic solvent. Thus, the expansion of the system, either because of the increase of temperature or the increase of the carbon dioxide mass fraction, has a smaller effect as compared to the case where the organic solvent is not a strong solvent for the polymer.

Conclusions

In this work the bubble and cloud point phase equilibrium data for the systems PCL + DCM + CO_2 were determined. Depending on the temperature, the polymer concentration, and the CO_2/DCM solvent organic mass ratio, V-L or L-L phase transitions may occur, each marked by the formation of a bubble or a cloud, respectively. An increase in temperature for a given mixture results in an increase in the necessary pressure to maintain the single phase. An increase in the solvent polarity leads to a shift of the V-L and L-L transitions to higher temperature and lower pressures. Moreover, the effect of the polymer mass fraction was investigated. It was experimentally observed that an increase in the polymer mass fraction led to an increase of the bubble and cloud point pressure values. In the case of bubble points, the observed increase in was more significant in systems rich in CO_2.

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