Phase Behavior of Binary and Ternary Systems Involving Carbon Dioxide, Propane, and Glycidyl Methacrylate at High Pressure

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This work reports experimental phase equilibrium data of binary and ternary systems involving carbon dioxide, propane, and glycidyl methacrylate (GMA). Phase equilibrium experimental data were obtained according to the static synthetic method using a variable volume view cell. The experiments covered the temperature range of (303 to 343) K, pressures up to 13 MPa, at several overall compositions. The experimental data were modeled with the Peng−Robinson equation of state (PR-EoS) with the conventional quadratic mixing rules. The EoS interaction parameters were fitted from binary systems and then used to predict the phase behavior of the ternary system. The results showed that, in the experimental range investigated, only vapor−liquid transitions were found and that the PR-EoS was capable of satisfactorily representing the experimental data.

Introduction

Supercritical fluid (SCF) technology has made tremendous advances in the past decade in terms of commercial applications and fundamental understanding of solution behavior[1] and has received great attention in the application and development of new processes and products.[2,3] Some of these applications are the use of SCFs as a solvent in chemical reactions,[4−7] polymer processing,[8−10] and environmental applications.[3,11] Studies have shown that carbon dioxide as a solvent can offer a “green” alternative for carrying out many types of chemistry often with significant process improvements in selectivity, conversion, or reaction rates.[1]

The supercritical CO_2 can be used as a way to obtain functionalized polymeric materials. The advantage of the modification using supercritical CO_2 process is the absence of toxic solvents and the possibility of CO_2 recycling. Because its tunable properties are highly attractive allowing reducing diffusion limitations in reaction systems and to reach a homogeneous distribution of active compounds in various porous matrixes, supercritical CO_2 will be widely used as a reaction medium.[12] Besides the common advantages of using supercritical CO_2 as a solvent medium, it is worth mentioning the ability of controlling the degree of grafting onto the polymeric matrix with a dry method or without an extrusion process.[13]

In polymer processing, the use of CO_2 as the solvent and swelling agent on the graft of monomers such as methyl methacrylate (MMA) and glycidyl methacrylate (GMA) onto the polymeric materials has been extensively described in the literature.[10,14−17] Glycidyl methacrylate is a desirable chemically reactive species, because its epoxy group could be converted into different kinds of functionalities through a ring-opening reaction by modifying polymeric materials, being important for various applications such as the dye ability of textiles, the improvement of adhesion for package industry, and the elaboration of membranes with specific properties.[14,18]

The knowledge of phase behavior of the reactional mixture places a crucial role in the selection of proper working conditions. Some works can be found in the literature regarding the phase behavior of some methylacrylates and acrylates in carbon dioxide, such as hexyl acrylate and hexyl methacrylate,[19] methyl methacrylate and acrylate,[20−23] and ethyl acrylate.[23] Despite the fact that the use of supercritical carbon dioxide for glycidyl methacrylate monomer processing has already been reported in the literature,[14,15,18] to our knowledge, phase behavior for this system has not been published yet. It should also be mentioned that, despite the benefits of supercritical carbon dioxide for polymer processing, the need for elevated pressure continues to be a challenge associated with its industrial utilization. A possible approach that potentially offers reducing operating pressures is polymerization in a liquid medium expanded with dense carbon dioxide. Over the last years, the use of compressed gases, like propane, as solvent or cosolvent has been employed in order to improve the solubility of a variety of solutes in carbon dioxide.[24−27]

In this context, the main objective of this work is to present new phase equilibrium experimental data of glycidyl methacrylate in compressed carbon dioxide and propane. Additionally, a ternary system composed of glycidyl methacrylatyte, carbon dioxide, and propane was also investigated. The phase equilibrium data were modeled with the Peng−Robinson equation of state (PR-EoS) with classical quadratic mixing rules.

Experimental Section and Modeling

Materials. Carbon dioxide (99.9 % purity in liquid phase, molar basis) and propane (99.5 % purity, molar basis) were purchased from White Martins S.A. Glycidyl methacrylate (GMA) (97 % purity, molar basis, Aldrich) was used without further purification. The critical properties (T_c and P_c) and acentric factor (ω) of pure compounds are presented in Table 1. When experimental values were not available in the literature,[28] they were predicted by the Marrero−Gani[29] (T_c and P_c) and Constantinou−Gani[30] (ω) group contribution methods.

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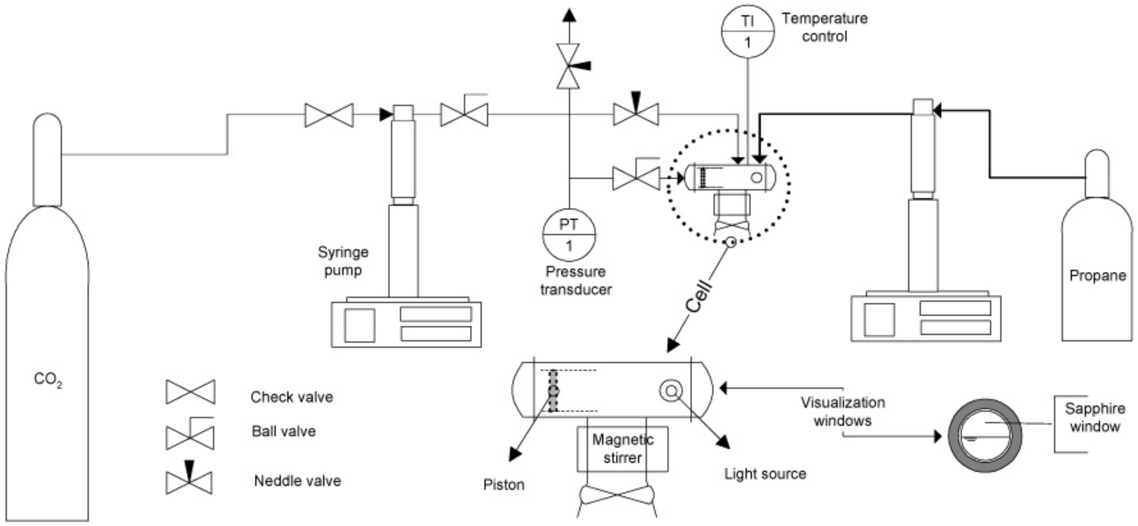

Figure 1. Schematic diagram of the experimental apparatus.

Table 1. Critical Properties and Acentric Factor of Pure Carbon Dioxide, Propane, and Glycidyl Methacrylate

compound	MM g/gmol	T_c K	P_c MPa	ω
CO_2[a]	44.01	304.21	7.383	0.2236
propane[a]	44.09	369.80	4.250	0.153
GMA[b]	142.00	644.13	3.299	0.2534

[a] From literature[28] [b] Estimated by the Marrero−Gani[29] and Constantinou−Gani[30] group contribution methods.

Apparatus and Experimental Procedure. Phase equilibrium experiments were measured 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;[27,31−34] hence, only a brief description is given. A schematic diagram of the apparatus is presented in Figure 1, which consists basically of a view cell with two sapphire windows for visual observations, an absolute pressure transducer (Smar, LD 301) with an accuracy of 0.012 MPa, a portable programmer (Smar, HT 201) for the pressure data acquisition, and two syringe pumps (ISCO 260D). The equilibrium cell has a maximum internal volume of 25 cm^3 and contains a movable piston, which permits the pressure control inside the cell. Phase transitions were recorded visually as bubble or dew points by varying the pressure behind the piston using CO_2 as the pressurizing fluid. The cell was equipped with a thermostatic bath and a proportional-integral-derivative controller (NOVUS, N480 model). The temperature in the cell was measured with an indicator (NOVUS, N1500 model) connected to a thermocouple (Fe−Co, with a precision of 0.5 K), which was in direct contact with the fluid mixture inside the cell body.

Depending on the desired overall composition, an amount of solute was weighed on a high-precision scale balance (Ohaus Analytical Standard with 0.0001 g accuracy) and loaded into the cell. Then the cell and all lines were flushed with low-pressure CO_2 to remove residual air. Afterward, the solvents (CO_2 or propane in the case of binary systems, and both for the ternary system with a molar ratio of 1:1) were pumped into the cell in order to reach the pre-established overall composition. The amount of solvent charged was monitored by the change in the volume of the transfer vessel of the pump. Then, the cell content was kept at continuous agitation with the help of a magnetic stirrer and a Teflon-coated stirring bar. After the desired temperature was reached, the cell pressure was increased by applying pressure on the back of the piston until the observation of a single phase. At this point, the system was allowed to stabilize at least 30 min, and the cell pressure was decreased slowly (typically 0.1 to 0.3 $MPa \cdot min^{-1}$) until incipient formation of a new phase. The equilibrium pressure was then recorded, after repetition of the experimental procedure at least four times. After completion of the measurement at a given temperature, the cell temperature was established at a new value, and the experimental procedure was repeated.

Through replicate measurements and the experience with the present apparatus, the uncertainty in pressure values is ascertained to be lower than 0.050 MPa. With regard to system composition, the mass of carbon dioxide and/or propane was carefully accounted for by the volume decay in the syringe pump. The syringe pump cylinder is a jacketed vessel that was coupled to an ultra thermostatic bath. The temperature uncertainty in the syringe pump vessel is lower than 0.5 K. To feed the solvent in the cell, the syringe pump was set to a determined pressure (15 MPa for both solvents) and temperature of 280.0 K and was maintained at this condition for at least 1 h for system stabilization. This condition was selected because experimental density values are available in the literature for CO_2.[35] For propane however density was calculated by the HBT equation.[28] When two solvents were present, they were independently fed into the cell by two syringe pumps, as schematically presented in Figure 1. The volume uncertainty in the syringe pump records is estimated to be lower than 0.005 cm^3, permitting us to estimate the uncertainty in molar fraction of about 0.005.

Modeling. The vapor−liquid equilibrium (VLE) experimental data were modeled with the PR-EoS with the classic quadratic mixing rules (two adjustable parameters: k_{ij} and l_{ij}).[36] The binary interaction parameters for the systems CO_2 + GMA and propane + GMA were estimated through the maximum likelihood method coupled to a bubble- or dew-point algorithm for calculation of VLE according to the Asselineau formulation[37,38] using a global temperature fitting procedure. To minimize the maximum likelihood objective function, it was employed the simulated annealing stochastic algorithm.[39,40] The parameters for the system CO_2 + propane were obtained by fitting[41] the experimental data reported in the literature.[42,43] The binary interaction parameters for all systems investigated in this work are presented in Table 2.

Table 2. Peng−Robinson EoS Binary Interaction Parameters Estimated Using a Global Temperature Fitting Procedure

system	k_{ij}	l_{ij}
CO_2 + GMA	0.0798	0.0210
CO_2 + propane[41]	0.1676	0.0751
propane + GMA	0.1527	−0.0363

Table 3. Vapor−Liquid Phase Transition Results for the System CO_2 (1) + GMA (2) of Mole Fraction *x*

	pressure ± σ/MPa				
x_1	T = 303 K	T = 313 K	T = 323 K	T = 333 K	T = 343 K
0.262	2.02 ± 0.01	2.31 ± 0.01	2.61 ± 0.01	2.93 ± 0.03	3.26 ± 0.04
0.519	4.11 ± 0.03	4.81 ± 0.02	5.54 ± 0.01	6.38 ± 0.01	7.24 ± 0.01
0.609	4.66 ± 0.01	5.58 ± 0.01	6.58 ± 0.01	7.63 ± 0.02	8.73 ± 0.03
0.764	5.73 ± 0.01	6.94 ± 0.04	8.30 ± 0.01	9.71 ± 0.01	11.24 ± 0.01
0.882	6.33 ± 0.02	7.75 ± 0.01	9.36 ± 0.01	11.09 ± 0.01	12.90 ± 0.01
0.948	6.46 ± 0.01	7.99 ± 0.03	9.67 ± 0.04	11.43 ± 0.04	13.10 ± 0.01
0.984	6.74 ± 0.01	8.25 ± 0.01	9.65[a] ± 0.01	11.17[a] ± 0.04	12.51[a] ± 0.05

[a] Dew points; all others are bubble points.

For the ternary system modeling, only binary information was taken into account. To carry out the predictions, the following main equations were considered:

$$N^{L}x_i + N^{V}y_i - z_i = 0; \quad i = 1, 2, ..., nc \tag{1}$$

$$y_i\hat{\phi}_i^{V} - x_i\hat{\phi}_i^{L} = 0; \quad i = 1, 2, ..., n_c \tag{2}$$

$$\sum_{i=1}^{n_c} x_i - \sum_{i=1}^{n_c} y_i = 0 \tag{3}$$

$$N^{L} + N^{V} - 1 = 0 \tag{4}$$

where N^L and N^V are the mole numbers of the liquid and vapor phases, respectively; x_i and y_i are the molar fractions of component *i* in the liquid and vapor phases, respectively; $\hat{\phi}_i^{V}$ and $\hat{\phi}_i^{L}$ are the fugacity coefficients of component *i* in the vapor and liquid phases, respectively; and n_c denotes the number of components. The following constraints must be considered:

$$\sum_{i=1}^{n_c} x_i = 1 \quad \text{and} \quad \sum_{i=1}^{n_c} y_i = 1 \tag{5}$$

The fugacity coefficients of the vapor and liquid phases were evaluated from the PR-EoS.[36] The equation system (eqs 1−4) was solved applying the Broyden method.[39]

Results and Discussion

In all tables reporting phase equilibrium experimental data, pressure values are in fact average values of at least four replicate measurements, and the experimental error of each condition is represented by the standard deviation of the replicates. The experimental compositions are expressed as the molar fraction of the lightest component in the liquid or vapor phases for bubble point (BP) or dew point (DP) phase transitions, respectively. A bubble point phase transition is characterized by the appearance of small bubbles appearing in the liquid bulk phase, whereas in a DP transition small drops are formed in the light phase.

Table 3 presents the experimental data obtained for the system CO_2 (1) + GMA (2). For this system, vapor−liquid phase transitions where observed for all temperatures (303 to 343 K) and compositions investigated. Bubble or dew points were observed depending on the mixture composition.

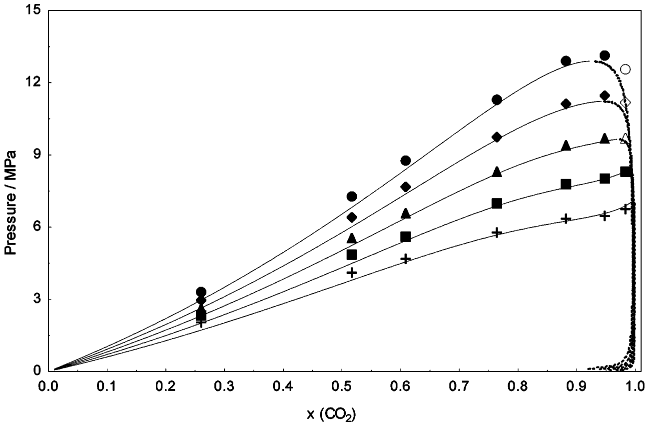

Figure 2. *P*−*x*−*y* equilibrium diagram for CO_2 + GMA system. Experimental data and calculated values from the PR-EoS: +, BP at 303 K; ■, BP at 313 K; ▲, BP at 323 K; △, DP at 323K; ◆, BP at 333 K; ◇, DP at 333 K; ●, BP at 343 K; ○, DP at 343 K; lines, PR-EOS.

Table 4. Vapor−Liquid Phase Transition Results for the System Propane (1) + GMA (2) of Mole Fraction *x*

	pressure ± σ/MPa			
x_1	T = 313 K	T = 323 K	T = 333 K	T = 343 K
0.764	1.32 ± 0.02	1.59 ± 0.01	1.92 ± 0.04	2.25 ± 0.01
0.829	1.36 ± 0.01	1.67 ± 0.01	1.99 ± 0.01	2.34 ± 0.01
0.883	1.28 ± 0.02	1.59 ± 0.03	1.92 ± 0.01	2.26 ± 0.02
0.928	1.27 ± 0.03	1.57 ± 0.02	1.91 ± 0.03	2.29 ± 0.02
0.980	1.32 ± 0.02	1.63 ± 0.02	1.97 ± 0.02	2.38 ± 0.02

Figure 2 presents the experimental data along with the correlation from the PR-EoS for the system CO_2 + GMA. One can observe from this figure a good agreement between the experimental and correlation results, indicating that the global temperature fitting procedure was adequate for obtaining the EoS binary interaction parameters. Lora and McHugh[20] reported equilibrium data for CO_2 + methyl methacrylate (MMA) system at 313, 353, and 378 K, presenting a similar behavior to the system investigated in this work. The authors also employed the PR-EoS to model the experimental data with satisfactory results.

According to Stradi et al.,[44] the main objective of performing binary system measurements is to provide information that would allow the prediction of phase behavior of multicomponent systems. In this sense, some experimental data points of the system propane + GMA were measured in order to estimate the related PR-EoS binary interaction parameters. Table 4 presents such experimental results, where it can be noticed that only bubble points were observed. It should also be noted from this table that the pressure transitions is quite invariant with propane composition in the experimental range investigated, with pressure transition values close to the vapor pressure of pure propane.

Table 5 presents the experimental data obtained for the ternary system CO_2 + propane + GMA. As depicted in Figure 3, bubble and dew points were recorded for this system. The goal was to investigate the influence of a cosolvent addition on the phase behavior of GMA + carbon dioxide. In Figure 3, it is possible to observe that the transition curves of the ternary system are located at much lower pressures in comparison to the CO_2 + GMA binary system, showing that the addition of propane increases the solubilization power of the solvent mixture. It should also be noted from this figure that a reasonable prediction of phase behavior of the ternary system was achieved from the binary systems information.

Table 5. Vapor−Liquid Phase Transition Results for the System CO_2 (1) + Propane (2) + GMA (3) of Mole Fraction x

		pressure ± σ/MPa				
x_1	x_2	$T = 303$ K	$T = 313$ K	$T = 323$ K	$T = 333$ K	$T = 343$ K
0.136	0.136	1.81 ± 0.01	2.00 ± 0.01	2.22 ± 0.01	2.42 ± 0.01	2.63 ± 0.04
0.290	0.290	2.69 ± 0.01	3.22 ± 0.01	3.74 ± 0.01	4.42 ± 0.01	5.08 ± 0.01
0.381	0.381	3.15 ± 0.01	3.80 ± 0.01	4.54 ± 0.01	5.31 ± 0.01	6.18 ± 0.03
0.441	0.441	3.58 ± 0.01	4.32 ± 0.01	5.09 ± 0.01	5.92 ± 0.01	6.80 ± 0.01
0.460	0.460	3.73 ± 0.02	4.44 ± 0.01	5.17 ± 0.02	6.01 ± 0.02	6.90 ± 0.02
0.474	0.474	3.90 ± 0.01	4.63 ± 0.01	5.44 ± 0.03	6.24 ± 0.03	7.10 ± 0.01
0.483	0.483	4.10 ± 0.01	4.86 ± 0.01	5.66 ± 0.01	6.44 ± 0.02	7.23 ± 0.02
0.492	0.492	4.19 ± 0.01	4.97 ± 0.01	5.76 ± 0.01	6.51 ± 0.01	7.10[a] ± 0.01
0.495	0.495	4.27 ± 0.01	5.05 ± 0.01	5.82 ± 0.01	6.49 ± 0.01	-

[a] Dew points; all others are bubble points.

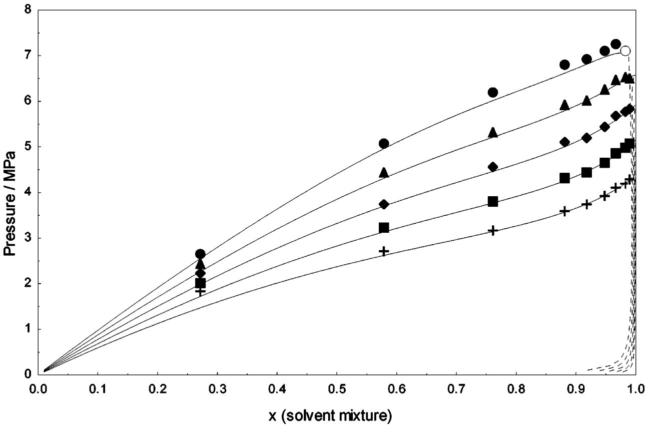

Figure 3. $P-x-y$ equilibrium diagram for CO_2 + propane + GMA ternary system (solvent mixture: CO_2 to propane molar ratio of 1:1). Experimental data and calculated values from the PR-EoS: +, BP at 303 K; ■, BP at 313 K; ◆, BP at 323 K; ▲, BP at 333 K; ●, BP at 343 K; ○, DP at 343 K; lines, PR-EOS.

Conclusions

In this work the phase behavior of binary and ternary systems involving CO_2, propane, and GMA were investigated in the temperature range (303 to 343) K and pressures up to 13 MPa. Vapor−liquid equilibrium phase transitions were observed as bubble and dew points. The PR-EoS with the classical quadratic mixing rules provided a satisfactory representation for the binary and ternary experimental data. The addition of propane to carbon dioxide significantly improved the solvent power.

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