J. Chem. Eng. Data **2010,** *55,* 2781–2785

Determination of Phase Equilibrium (Solid−Liquid−Gas) in Poly-(ε-caprolactone)−Carbon Dioxide Systems

Esther de Paz, Ángel Martín,* Soraya Rodríguez-Rojo, Javier Herreras, and María José Cocero

High Pressure Processes Group, Department of Chemical Engineering and Environmental Technology, University of Valladolid, Prado de la Magdalena s/n 47011 Valladolid, Spain

Solid−liquid−gas equilibrium of poly-(ε-caprolactone)−carbon dioxide systems at high pressure has been determined by visual determination of the first melting point using a static apparatus. Measurements have been performed with poly-(ε-caprolactones) of three different molecular weights: 4000 $\text{g}\cdot\text{mol}^{-1}$, 10 000 $\text{g}\cdot\text{mol}^{-1}$, and 25 000 $\text{g}\cdot\text{mol}^{-1}$. The determined SLG equilibrium lines show a temperature maximum at low pressures (0.5 Pa $< P <$ 1.6 MPa) and a temperature minimum at moderate pressures (8 MPa $< P <$ 10 MPa). The maximum reduction of melting temperature ranges from (12.5 to 16.0) K depending on the molecular weight of the polymer. A thermodynamic model based on the PC-SAFT equation of state has been developed to describe experimental data.

Introduction

Controlled release formulations are often prepared by encapsulation of the active compound in a natural or biodegradable polymer. Polymeric nanocarriers can show several desirable properties including controlled release of the active compound, long longevity in the body, or even specific targeting to certain disease sites.[1] Polyesters such as poly(lactic acid) (PLA) or poly(glycolic acid) (PLG) have been widely employed to prepare carriers for controlled release of drugs and proteins. These polymers degrade by bulk hydrolysis of ester bonds, and their rate of degradation depends on several parameters such as chemical structure, crystallinity, hydrophobicity, and molecular weight.[2] The successful use of these polymers in pharmaceutical applications has led to the evaluation of other aliphatic polyesters such as poly-(ε-caprolactone) (PCL).

Poly-(ε-caprolactone) is a synthetic biocompatible semicrystalline polymer. PCL exhibits a low glass transition temperature (from (−60 to −10) °C, depending on its molecular weight) which imparts a rubbery characteristic to the material, which results in high permeability. This property has been exploited for delivery of low molecular weight drugs such as steroids and vaccines.[3] PCL has also been used as a platform for high molecular weight substances as for example proteins where protection against degradation provided by PCL has been proved to be better than the protection achieved with other polyesters.[4,5]

Precipitation processes based on the use of supercritical fluids, and in particular of supercritical carbon dioxide, have been successfully applied to produce polymeric carriers. Different techniques have been developed, including Rapid Expansion of Supercritical Solutions (RESS), Supercritical AntiSolvent (SAS), and Particles from Gas Saturated Solutions (PGSS), which present significant advantages over other precipitation techniques including the possibility to process the material in an inert and nontoxic medium and an enhanced control over particle size and morphology.[6] To design these processes and optimize the operating conditions, a detailed knowledge of the phase behavior of polymer + supercritical fluid mixtures is required.

It is well-known that supercritical carbon dioxide interacts with polymers acting as a plasticizing and swelling agent and reduces significantly the glass transition and melting temperatures of the polymer.[7] Knowledge of Solid−Liquid−Gas (SLG) phase behavior of polymer + CO_2 mixtures is therefore very important for developing formulation processes because it determines the conditions in which solid particles can actually be produced, as well as near-melting conditions which may be favorable for impregnation processes.

Several articles deal with the determination of the phase behavior of PCL + CO_2 mixtures. Cotugno et al.[8] reported the solubility of near-critical CO_2 in PCL (molecular weight, 80 000 $\text{g}\cdot\text{mol}^{-1}$; melting temperature, 58 °C) at high temperature (from (70 to 85) °C). Domingo et al.[9] measured the solubility of a polymer blend (PMMA/PCL) in supercritical CO_2 without and with cosolvents (acetone, dichloromethane, and ethanol). Rodríguez-Rojo et al.[10] determined the solubility of PCL with an average molecular weight of 1000 $\text{g}\cdot\text{mol}^{-1}$ in CO_2 using ethanol as cosolvent. Leeke et al.[11] measured the solubility of supercritical CO_2 in the polymer in the temperature range from (40 to 60) °C with pressures up to 20 MPa. Lian et al.[12] determined the SLG phase behavior of PCL with average mol wt of 4000 $\text{g}\cdot\text{mol}^{-1}$ with CO_2.

In this work, the SLG phase behavior of PCL and CO_2 at high pressure (P = (0.1 to 25) MPa) is reported. Measurements have been carried out using PCL with three different molecular weights: 4000 $\text{g}\cdot\text{mol}^{-1}$, 10 000 $\text{g}\cdot\text{mol}^{-1}$, and 25 000 $\text{g}\cdot\text{mol}^{-1}$. Furthermore, a thermodynamic model of the phase behavior of CO_2 + PCL mixtures based on the PC-SAFT equation of state[13] is presented.

Experimental Section

Materials. Carbon dioxide (purity: 99.5 %) was provided by S. E. Carburos Metálicos S. A. (Spain). Poly-(ε-caprolactones) were kindly supplied by Solvay Caprolactones (Solvay Interox Ltd., United Kingdom). Three different commercial poly-(ε-

---

* Corresponding author. E-mail: mamaan@iq.uva.es.

10.1021/je900997t

Table 1. Physical Properties of Poly-(ε-caprolactones) Used in This Work[a]

PCL	MW ($g\cdot mol^{-1}$)	T_m (°C)
CAPA 2403D	4000	50 to 60
CAPA 6100	10000	58 to 60
CAPA 6250	25000	60to 70

[a] Data provided by the supplier.

caprolactones) were used: CAPA 2043D, CAPA 6100, and CAPA 6250. Physical properties of PCLs used in this work are summarized in Table 1. All products were used as received.

Equipment. A schematic diagram of the equipment used for melting point determinations is shown in Figure 1. The main part of the equipment is an optical cell (SITEC 740.2120) with an inner volume of 25 mL. Maximum operating conditions inside the cell are $P = 50$ MPa and $T = 473$ K. The cell has two opposite sapphire windows. Through one of them, a cold light lamp is situated to allow the visualization of the different processes taking place inside the cell aided by a CCD camcorder (Eurotechnica Ingenieurbüro GMBH) connected to a personal computer. The internal temperature of the cell is controlled by a PID temperature controller (OMRON E5GN) acting over an electrical jacket and measuring the temperature with a J type thermocouple (SITEC 770.5131-22, accuracy 0.1 K). Pressure is measured with a membrane pressure meter (DESIN TPR-18/V2, accuracy 0.01 MPa). The system also has a manual pressure generator (SITEC 750.1060) which adjusted the system volume and a diaphragm pump (Dosapro).

Method. The melting point of PCL with CO_2 at high pressure was measured by visually determining the temperature at which melting started at a certain fixed pressure, according to the first melting point method.[12] For doing so, a small amount of PCL was put in a glass vial and introduced in the optical cell. Afterward, the cell was flushed with CO_2 to remove air, and the cell was filled with CO_2 and pressurized up to the desired operating pressure by using the diaphragm pump. Then the cell was gradually heated with the electrical jacket until melting of the PCL sample was observed with the CCD camcorder. After each temperature variation, temperature and pressure were maintained constant during a minimum of 30 min to ensure system equilibration. During the heating process, pressure was maintained constant within ± 0.1 MPa by manipulation of the manual pressure generator. Preliminary experiments showed that melting temperatures visually determined with this method were reproducible within ± 0.5 K.

Thermodynamic Model

The PC-SAFT Equation of State considers molecules to be constituted by chains of freely jointed spherical segments. This equation was developed in terms of the residual Helmholtz free energy a^{res}, which can be calculated as the sum of three contributions, as presented in eq 1

$$a^{res} = a^{hc} + a^{disp} + a^{assoc} \tag{1}$$

In this equation, a^{hc} accounts for the repulsion of the chainlike molecule, using the hard-chain expression derived by Chapman et al.;[14] a^{disp} accounts for the dispersion forces due to attraction between temporarily induced dipoles; and a^{assoc} accounts for the association between molecules, described by the association term of the original SAFT Equation of State.[15] Full details about the calculation of these contributions to the residual Helmholtz energy were provided by Gross and Sadowski[13] and by Chapman et al.[14]

Within this framework, nonassociating molecules are described by three parameters: the number of segments per chain m, the segment diameter σ, and the depth of the pair potential ε/k_b. Conventional mixing rules can be used for the parameters σ and ε/k_b

$$\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j) \tag{2}$$

$$\varepsilon_{ij} = (\varepsilon_i \cdot \varepsilon_j)^{0.5} \cdot (1 - k_{ij}) \tag{3}$$

where k_b and k_{ij} are Boltzmann's constant and binary interaction parameter, respectively.

For calculation of SLG equilibria, this equation of state has to be applied to solve the condition of equality of fugacity of each component in each phase

$$f_i^S = f_i^L = f_i^G \tag{4}$$

As with most equations of state, PC-SAFT can only be used to calculate the fugacity of fluid phases and not of solid phases. As an approximation, the fugacity of the solid phase can be calculated as a function of the fugacity of a reference, subcooled liquid f^{SCL} with the following equation, which is strictly valid in the triple point of the substance[16]

$$f_i^S(T,P) = f_i^{SCL}(T,P)\exp\left[\frac{(v_2^{S} - v_2^{SCL})(P - P^0)}{RT} + \frac{\Delta h^{fus}}{RT^0}\left(1 - \frac{T^0}{T}\right)\right] \tag{5}$$

where T^0 and Δh^{fus} are the melting temperature and heat of fusion of the PCL at the triple point pressure P^0 which can be approximated with good accuracy by the corresponding values at normal conditions. v_2^S and v_2^{SCL} are the molar volumes of solid and subcooled liquid polymer, respectively.

Results and Discussion

Experimental results obtained in this work are presented in Tables 2, 3, and 4 and in Figures 2, 3, and 4. It can be seen that the melting point curves obtained with the three investigated PCLs have a similar shape: at low pressures, there is a certain increase of melting temperature when pressure is increased. In the case of CAPA 2403D, melting temperature increases as much as 3.5 K, while in the case of the other two PCLs the extent of this increase is 1 K. For CAPA 2043D, the maximum melting temperature is observed at 1.6 MPa. In the case of CAPA 6100 and CAPA 6250, this temperature is observed at (0.8 and 0.5) MPa, respectively. In the pressure range 1 MPa < P < 8 MPa, melting temperature strongly decreases with pressures with a nearly linear variation. At higher pressures, melting temperature either shows no variation or increases slightly when pressure is increased. The maximum melting temperature depression is 12.5 K in the case of CAPA 2403D, 15.5 K in the case of CAPA 6100, and 16.0 K in the case of CAPA 6250.

Lian et al.[12] also determined the SLG phase equilibria of a poly-(ε-caprolactone) with average molecular weight of 4000 $g\cdot mol^{-1}$, equivalent to that of CAPA 2043D. For comparison purposes, in Figure 2 the results of these authors are represented together with results obtained in this work. It can be seen that the results of Lian et al. present the same shape of data obtained in this work. Both data sets report the same melting temperature at ambient conditions (327 K) and a similar maximum melting temperature ($T = 330.5$ K at $P = 1.6$ MPa in this work and $T = 332.2$ K at $P = 0.7$ MPa in the data set of Lian et al.), and

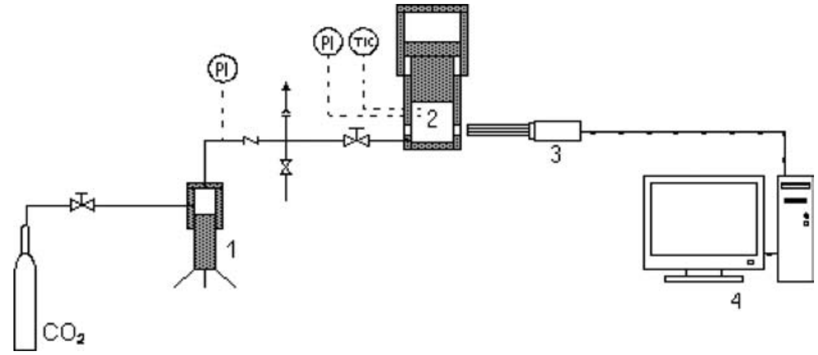

Figure 1. Schematic diagram of the measurement equipment. 1, Manual pressure generator; 2, high-pressure optical cell; 3, CCD camera system; 4, personal computer.

Table 2. Experimental Solid−Liquid−Gas Phase Equilibrium Results of CAPA 2403D (Molecular Weight: 4000 g·mol^{-1}) + CO_2 Mixtures[a]

P/MPa	*T*/K	*P*/MPa	*T*/K
0.1	327.0	12.1	315.0
0.1	326.0	12.6	313.5
1.0	327.5	13.1	315.0
1.2	330.0	14.0	314.0
1.6	330.5	15.2	314.0
1.9	326.5	16.5	315.0
2.1	326.0	18.9	315.0
3.0	324.0	20.1	314.0
4.2	322.0	21.1	315.0
5.3	320.5	22.3	314.0
6.2	320.5	23.4	315.0
7.4	317.0	24.2	315.5
8.4	314.5	25.6	315.0
9.3	314.5	27.1	315.0
10.4	315.0		

[a] Experimental uncertainties: ± 0.5 K (temperature), ± 0.1 MPa (pressure).

Table 3. Experimental Solid−Liquid−Gas Phase Equilibrium Results of CAPA 6100 (Molecular Weight: 10 000 g·mol^{-1}) + CO_2 Mixtures[a]

P/MPa	*T*/K	*P*/MPa	*T*/K
0.1	331.0	9.3	313.0
0.1	331.0	10.1	314.0
0.6	332.0	10.6	315.0
0.9	332.0	10.6	315.0
1.1	331.5	10.6	315.0
2.0	330.5	11.6	316.0
2.5	330.0	12.5	314.0
3.6	328.0	14.1	315.0
5.0	323.0	15.3	316.0
5.3	325.5	16.2	316.0
6.3	321.0	17.1	315.0
7.4	318.5	19.3	315.0
8.3	316.0	20.1	316.0
8.3	316.0	21.6	316.0
8.9	314.0	22.8	315.5
9.1	314.0	25.1	316.0

[a] Experimental uncertainties: ± 0.5 K (temperature), ± 0.1 MPa (pressure).

the slope of the *T* vs *P* curve in the region of moderate pressures (1 MPa to 8 MPa) is also similar in both data sets. However, significant differences can be observed between the two data sets in the region of high pressure because Lian et al. observed a minimum melting temperature of about 310 K, which is 4.5 K lower than that observed in this work. It is worth mentioning that the PCLs used in the two works were obtained from different suppliers: Solvay Policaprolactones in this work and Dow Chemicals in the work of Lian et al. It is therefore possible that these products have differences in properties such as the exact value of the mean molecular weight or the polydispersity index which could justify the observed differences in the melting behavior.

Table 4. Experimental Solid−Liquid−Gas Phase Equilibrium Results of CAPA 6250 (Molecular Weight: 25 000 g·mol^{-1}) + CO_2 Mixtures[a]

P/MPa	*T*/K	*P*/MPa	*T*/K
0.1	335.0	6.1	321.0
0.1	334.0	7.1	318.5
0.6	336.0	8.3	318.5
0.8	335.5	9.4	319.0
1.5	334.0	10.2	318.0
2.2	332.5	11.2	319.5
3.1	330.0	12.1	318.5
4.6	326.5	13.1	319.0
5.2	325.5	14.1	320.5

[a] Experimental uncertainties: ± 0.5 K (temperature), ± 0.1 MPa (pressure).

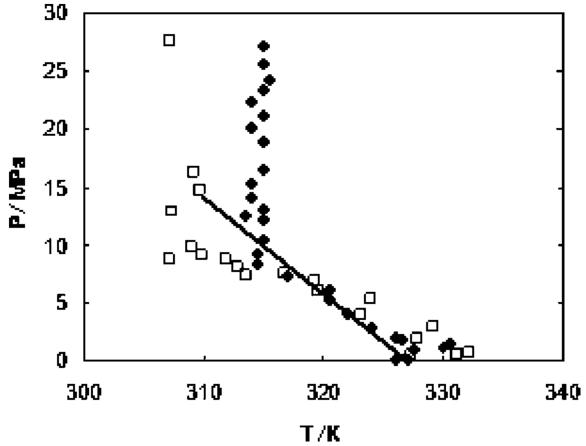

Figure 2. SLG equilibrium of PCL−CO_2 systems: results with PCL with molecular weight 4000 g·mol^{-1} (CAPA 2403D). Symbols: ◆, experimental results; □, literature data;[8] continuous line, model results.

A similar shape of the SLG equilibrium lines with maximum and minimum melting temperatures was observed by Weidner et al. for the system carbon dioxide + polyethylene glycol.[17] The minimum melting temperature phenomenon can be easily explained by considering the balanced effects of the dissolution of CO_2 into the polymer, which tends to reduce the melting temperature, and hydrostatic pressure, which tends to increase this temperature. Indeed, the solubility of CO_2 in most molten polymers can be very high, and at moderate pressures it increases rapidly and almost linearly when pressure is increased. Over a certain pressure, the solubility of CO_2 increases by a very small extent even if large pressure increases are applied, resulting in an almost vertical *P* vs x_{CO2} equilibrium line.[11]

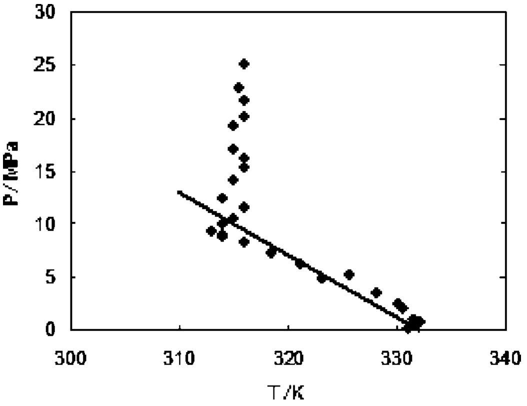

Figure 3. SLG equilibrium of PCL−CO_2 systems: results with PCL with molecular weight 10 000 g·mol^{-1} (CAPA 6100). Symbols, experimental results; continuous line, model results.

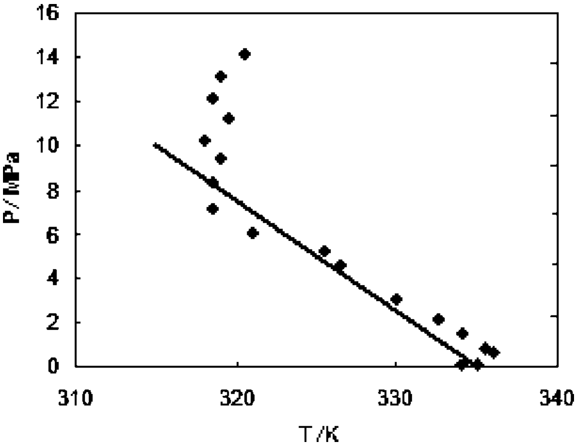

Figure 4. SLG equilibrium of PCL−CO_2 systems: results with PCL with molecular weight 25 000 g·mol^{-1} (CAPA 6250). Symbols, experimental results; continuous line, model results.

Therefore, it can be argued that at moderate pressures the effect of CO_2 solubilization prevails, hence the important reduction of melting temperature in this pressure range, while at high pressures the solubility of CO_2 in the molten polymer increases by a small extent when pressure is increased. Therefore, the hydrostatic pressure effect prevails. However, the maximum melting temperature phenomenon cannot be easily explained by thermodynamic considerations. In a detailed thermodynamic analysis, de Loos[18] concluded that in a binary system such behavior is possible only if the solubility of CO_2 in the solid phase is higher than in the liquid phase. Nevertheless, de Loos pointed out that such behavior is very rare, as in most cases a negligible solubility of CO_2 in the solid is expected at low pressures.

On the other hand, Lian et al.,[12] who also observed a maximum melting temperature in CO_2 + PCL systems, attributed this phenomenon to lamellar thickening of PCL due to the enhanced polymer-chain mobility in the CO_2-exposed amorphous regions. This explanation was based on the experimental observations of Siheh and Yang,[19] who observed this phenomenon in PCL exposed to CO_2 at high pressure by application of Differential Scanning Calorimetry (DSC) and Small-Angle X-ray Scattering (SAXS). However, it must be pointed out that according to Siheh and Yang[19] these modifications in the crystalline structure of PCL only took place when the polymer was exposed to CO_2 at moderately high pressures ($P > 3.6$ MPa). A similar behavior has been observed with other polymers: López-Periago et al.[20] found that CO_2 could cause a solvent-induced crystallization in polylactic acid exposed to CO_2 at temperatures below the glass transition temperature. This crystallization resulted in an increase of the melting temperature and melting enthalpy, but high CO_2 pressure was required (10 MPa < P < 20 MPa)

Table 5. PC-SAFT EoS Pure Component Properties Considered in This Work

	m	σ Å	ε/k_b K	ρ kg·m^{-3}	ΔH_{fus} J·g^{-1}
CO_2	2.0729	2.7852	169.21		
PCL	0.0396·MW	3.3908	235.67	1140	76.9

Another possible explanation of the maximum melting temperature phenomenon arises from the fact that it has only been observed with polymers (e.g., PEG by Weidner et al.[17] or PCL by Lian et al.[12] and in this work). Indeed, SLG measurements with other substances such as tristearin, tripalmitin,[18] tetradecanid acid, hexadecanoic acid, or 1-hexadecanol[21] do not show a temperature maximum. It is possible that the maximum melting point phenomenon is a consequence of PCL + CO_2 mixtures not being binary systems due to the polydispersity of the polymer. CO_2 may be able to selectively extract low molecular weight oligomers from the polymer which act as plasticizing agents, thus causing an increase in the melting point.

A thermodynamic model of the phase equilibrium of (PCL + CO_2) mixtures based on the PC-SAFT EoS[13] has been developed in this work. Pure component parameters required by this model are presented in Table 5. The parameters of CO_2 have been taken from the literature,[13] while the parameters of PCL have been estimated with the group contribution method developed by Tihic et al.[22] As shown in this table, parameter m of PCL depends on the molecular weight of the polymer, which enables using this set of parameters with PCLs of different molecular weights.

As previously described, to apply the PC-SAFT EoS to mixtures the binary interaction parameter must be calculated. The interaction parameter between CO_2 and PCL has been calculated by correlation of vapor−liquid equilibrium data reported by Cotugno et al.[8] in the temperature range 343 K < T < 358 K. The correlation has been performed by minimization of the Average Absolute Pressure Deviation (AAPD) between experimental and calculated bubble point pressures, according to the objective function presented in eq 6. With this procedure, the following expression has been obtained for the binary interaction coefficient between CO_2 and PCL: $k_{12} = 177.966/T - 0.4558$. With this parametrization, the maximum deviation between experimental LV bubble point pressures and PC-SAFT calculations is AAPD = 6.8 %.

$$\mathrm{AAPD} = \frac{100}{n_{\mathrm{exp}}} \sum_{i}^{n_{\mathrm{exp}}} \frac{|P^{\mathrm{calc}} - P^{\mathrm{exp}}|}{P^{\mathrm{exp}}} \qquad (6)$$

Density and heat of fusion data of PCLs required for SLG equilibrium calculations with eq 5 were taken from the literature[8,19] and are listed in Table 5. Results of equilibrium calculations with the PC-SAFT equation are shown in Figures 2, 3, and 4 together with experimental results. It can be seen that the model correctly describes the decrease of melting temperature with increasing pressure in the region of moderate pressures (P < 10 MPa). It can be therefore used to estimate the melting temperature of PCLs of different molecular weights in this pressure range, which is of interest for several supercritical precipitation techniques such as SAS or PGSS. However, the model fails to predict the minimum melting point temperature and the increase of melting point with pressure at high pressures. This is probably due to the simplicity of the model used to represent the solid phase (eq 5). A similar limitation of this model was found in the modeling of SLG equilibrium of the system polyethylene glycol + CO_2.[23]

Conclusions

The solid−liquid−gas equilibrium in poly-(ε-caprolactone) + CO_2 systems has been determined. Measurements have been carried out with PCLs of three different molecular weights: 4000 $g\cdot mol^{-1}$, 10 000 $g\cdot mol^{-1}$, and 25 000 $g\cdot mol^{-1}$. The experimentally determined SLG equilibrium curves show both a temperature maximum at low pressures (0.5 MPa $< P <$ 1.6 MPa) and a temperature minimum at moderate pressures (8 MPa $< P <$ 10 MPa). The maximum reduction in melting temperature is 12.5 K in the case of PCL 4000 $g\cdot mol^{-1}$, 15.5 K in the case PCL 10 000 $g\cdot mol^{-1}$, and 16.0 K in the case of PCL 25 000 $g\cdot mol^{-1}$. A thermodynamic model based on the PC-SAFT equation of state has been developed to describe experimental data. The model correctly predicts the solubility of CO_2 in the molten polymer as well as the melting temperature at pressures below the pressure of the minimum melting temperature, but it is not able to describe the variation of melting temperature at higher pressures.

Acknowledgment

The authors thank Solvay Caprolactones for providing the poly-(ε-caprolactones) used in this work.

Literature Cited

(1) Torchilin, V. Multifunctional and stimuli-sensitive pharmaceutical nanocarriers. *Eur. J. Pharm. Biopharm.* **2009**, *71*, 431–444.

(2) Barbato, F.; La Rotonda, M. I.; Maglio, G.; Palumbo, R.; Quaglia, F. Biodegradable microspheres of novel segmented poly(ether-ester-amide)s based on poly(ϵ-caprolactone) for the delivery of bioactive compounds. *Biomaterials* **2001**, *22*, 1371–1378.

(3) Coombes, A. G. A.; Rizzi, S. C.; Williamson, M.; Barralet, J. E.; Downes, S.; Wallacee, W. A. Precipitation casting of polycaprolactone for applications in tissue engineering and drug delivery. *Biomaterials* **2004**, *25*, 315–325.

(4) Yang, Y. Y.; Chung, T. S.; Ping, N. Morphology, drug distribution, and in vitro release profiles of biodegradable polymeric microspheres containing protein fabricated by double-emulsion solvent extraction/evaporation method. *Biomaterials* **2001**, *22*, 231–241.

(5) Youan, B. B. C.; Jackson, T. L.; Dickens, L.; Hernández, C.; Owusu-Ababio, G. Protein release profiles and morphology of biodegradable microcapsules containing an oily core. *J. Controlled Release* **2001**, *76*, 313–326.

(6) Cocero, M. J.; Martín, Á.; Mattea, F.; Varona, S. Encapsulation and co-precipitation processes with supercritical fluids: fundamentals and applications. *J. Supercrit. Fluids* **2009**, *47*, 546–555.

(7) Kikic, I. Polymer-supercritical fluid interactions. *J. Supercrit. Fluids* **2009**, *47*, 458–465.

(8) Cotugno, S.; Di Maio, E.; Ciardiello, C.; Iannace, S.; Mensitieri, G.; Nicolais, L. Sorption thermodymanics and mutual diffusivity of carbon dioxide in molten polycaprolactone. *Ind. Eng. Chem. Res.* **2003**, *42*, 4398–4405.

(9) Domingo, C.; Vega, A.; Fanovich, M. A.; Elvira, C.; Subra, P. Behavior of poly(methyl methacrylate)-based systems in supercritical CO_2 and CO_2 plus cosolvent: Solubility measurements and process assessment. *J. Appl. Polym. Sci.* **2003**, *90*, 3652–3659.

(10) Rodríguez-Rojo, S.; Martín, Á.; Sáez-Calvo, E.; Cocero, M. J. Solubility of polycaprolactone in supercritical carbon dioxide with ethanol as cosolvent. *J. Chem. Eng. Data* **2009**, *54*, 962–965.

(11) Leeke, G. A.; Cai, J.; Jenkins, M. Solubility of Supercritical Carbon Dioxide in Polycaprolactone (CAPA 6800) at 313 and 333 K. *J. Chem. Eng. Data* **2006**, *51*, 1877–1879.

(12) Lian, Z.; Epstein, S. A.; Blenk, C. W.; Shine, A. D. Carbon dioxide-induced melting point depression of biodegradable semicrystalline polymers. *J. Supercrit. Fluids* **2006**, *39*, 107–117.

(13) Gross, J.; Sadowski, G. Perturbed-Chain SAFT: An equation of state based on a perturbation theory for chain molecules. *Ind. Eng. Chem. Res.* **2001**, *40*, 1224–1260.

(14) Chapman, W. G.; Jackson, G.; Gubbins, K. E. Phase equilibria of associating fluids - Spherical molecules with multiple bonding sites. *Mol. Phys.* **1988**, *65*, 1–31.

(15) Chapman, W. G.; Gubbins, K. E.; Jackson, G; Radosz, M. New reference equation of state for associating liquids. *Ind. Eng. Chem. Res.* **1990**, *29*, 1709–1721.

(16) Prausnitz, J. M.; Lichtenhaler, R. N.; Azevedo, E. G. *Molecular Thermodynamics of Fluid-Phase Equilibria*, 3rd. ed.; Prentice Hall PTR: New Jersey, 1998.

(17) Weidner, E.; Wiesmet, Z.; Knez, Z.; Skerget, M. Phase equilibrium (solid-liquid-gas) in polyethylene glycol - carbon dioxide systems. *J. Supercrit. Fluids* **1997**, *10*, 139–147.

(18) De Loos, T. W. On the phase behaviour of asymmetric systems: The three-phase curve solid-liquid-gas. *J. Supercrit. Fluids* **2006**, *39*, 154–159.

(19) Shieh, Y.-T.; Yang, H.-S. Morphological changes of polycaprolactone with high-pressure CO_2 treatment. *J. Supercrit. Fluids* **2005**, *33*, 183–192.

(20) López-Periago, A.; García-González, C. A.; Domingo, C. Solvent and thermal induced crystallization of poly-L-lactic acid in supercritical CO_2 medium. *J. Appl. Polym. Sci.* **2009**, *111*, 291–300.

(21) Uchida, H.; Kamijo, T. Measurement and correlation of the solid-liquid-gas equilibria for carbon dioxide+normal chain saturated aliphatic hydrocarbon systems. *J. Supercrit. Fluids* **2009**, *51*, 136–141.

(22) Tihic, A.; Kontogeorgis, G. M.; von Solms, N.; Michelsen, M. L.; Constantinous, L. A predictive group-contribution simplified PC-SAFT equation of state: application to polymer systems. *Ind. Eng. Chem. Res.* **2008**, *47*, 5092–5101.

(23) Martín, Á.; Pham, H.-M.; Kilzer, A.; Kareth, S.; Weidner, E. Phase equilibria of carbon dioxide + poly ethylene glycol + water mixtures at high pressure: Measurements and modelling. *Fluid Phase Equilib.* **2009**, *286*, 162–169.

Received for review November 24, 2009. Accepted January 20, 2010. The authors thank Junta de Castilla y León (Spain) for funding this research (project GR-11). A. Martín thanks the Alexander von Humboldt foundation (Germany) for a postdoctoral research grant.

JE900997T