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Bubble and Cloud Points of the System Poly(L-lactic acid) + Carbon Dioxide + Dichloromethane

Constantinos G. Kalogiannis and Constantinos G. Panayiotou*

Department of Chemical Engineering, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece

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Experimental data for the phase behavior of poly(L-lactic acid) (PLA) in mixtures of dichloromethane and carbon dioxide over a range of external conditions are presented. Cloud point pressures were measured using a variable-volume view cell as functions of temperature, dichloromethane-to-carbon dioxide ratio, and concentration of PLA. A high-molecular-weight (M_w 189 000) PLA was used in all studies and at mass fractions of 0.01, 0.02, and 0.03. For adequate control of the carbon dioxide-to-dichloromethane ratio, a new experimental procedure was employed that allows for good control of the composition. To ascertain the validity of the new experimental procedure, the binary system of carbon dioxide + dichloromethane was studied, and its results were compared to literature values.

Introduction

Processes with supercritical fluids have attracted particular attention over the last few decades. Their applications have a wide scope such as extraction, separation, fractionation, reaction, processing of drugs and polymers, micronisation, and foam formation. They may be employed as solvents or nonsolvents, are environmentally friendly, less hazardous and more flexible than common organic solvents, and comply with modern standards of the drug and food industry.[1] In the past few years, attempts have been made to produce microparticles of biodegradable polymers and to encapsulate drugs in such polymers so that they may be used as agents for the administration of drugs to the human body.[2,3] Carbon dioxide is the number-one fluid employed as a supercritical nonsolvent in such cases because of its availability, mild critical point, and environmentally friendly profile.[4] Microparticles of PLA have been produced,[5] and the encapsulation of drugs in this polymer has been attempted successfully.[6,7]

Dichloromethane is a good solvent for PLA and has been used in all of the above-mentioned applications. Knowledge of the phase behavior of the system polymer + organic solvent + supercritical antisolvent is important for the determination of the best operating conditions for the production of microparticles of biodegradable polymers and for the encapsulation of drugs in such polymers.

In this work, the points where the separation of the single phase occurs were studied for the system PLA + carbon dioxide + dichloromethane in a high-pressure apparatus with a variable-volume view cell. Both liquid−vapor (L−V) and liquid−liquid (L−L) transitions occur, depending on the temperature and the composition of the mixtures. This system was also studied by Lee et al.[8] but at different conditions. Their findings are compared with our results, and conclusions are drawn. Our work along with the work of Lee et al.[8] gives a clearer picture of this important ternary system over a broader range of conditions.

Experimental Section

Materials. Poly(L-lactic acid) (PLA) (M_w 189 000, polydispersity 2.31) was purchased from Galactic Laboratories (Belgium) and was used without further purification. Instrument-grade carbon dioxide (purity 99.99%) was supplied by Air Liquide Mediterranée (Vitrolles, France). Analytical-grade dichloromethane (99.9% purity) was purchased from Riedel-de Haen (Germany).

Apparatus and Procedure. The phase behavior of the mixtures of PLA, CO_2, and dichloromethane was studied with a high-pressure apparatus equipped with a variable-volume view cell. A schematic diagram of the apparatus is shown in Figure 1. The main advantage of this apparatus is that the concentration of the system can be kept constant during the experiment.[9] The apparatus consists of a high-pressure view cell with a sapphire window (4) and a camera (6) that monitors and records the phase transitions. A magnetic stirrer (3) provides sufficient agitation for a thorough mixing of the components inside the cell. The cell itself is cylindrical with internal diameter 1.74 cm, height 11.25 cm, and internal volume 26.75 cm^3. The system pressure is measured with a WIKA transducer with an uncertainty of 0.1 bar. The system temperature is controlled via a silicon heating tape and measured with a Pt100 thermocouple probe inserted into the cell. A key feature of this apparatus is that the pressure is measured directly on the solvent side. The dead volumes of all the tubing, the magnetic stirrer, and the temperature probe have been determined because they must be known prior to phase equilibrium measurements. Moreover, care was exercised to keep the tubing and the pressure gauge clean because polymer may plug it during depressurization, which is why all of the tubing was purged with dichloromethane after each experiment.

The experimental procedure is as follows. Initially, a known mass of polymer with an uncertainty of 10^{-4} g is inserted into the cell along with a stirring magnet bar. Afterward, the cell is purged several times with CO_2 to ensure that there is no entrapped air left. The cell is then filled with CO_2 (1) at a specific pressure and temperature. Valve 5b isolates the system, and the CO_2 feed is stopped.

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* Corresponding author. E-mail: cpanayio@auth.gr.

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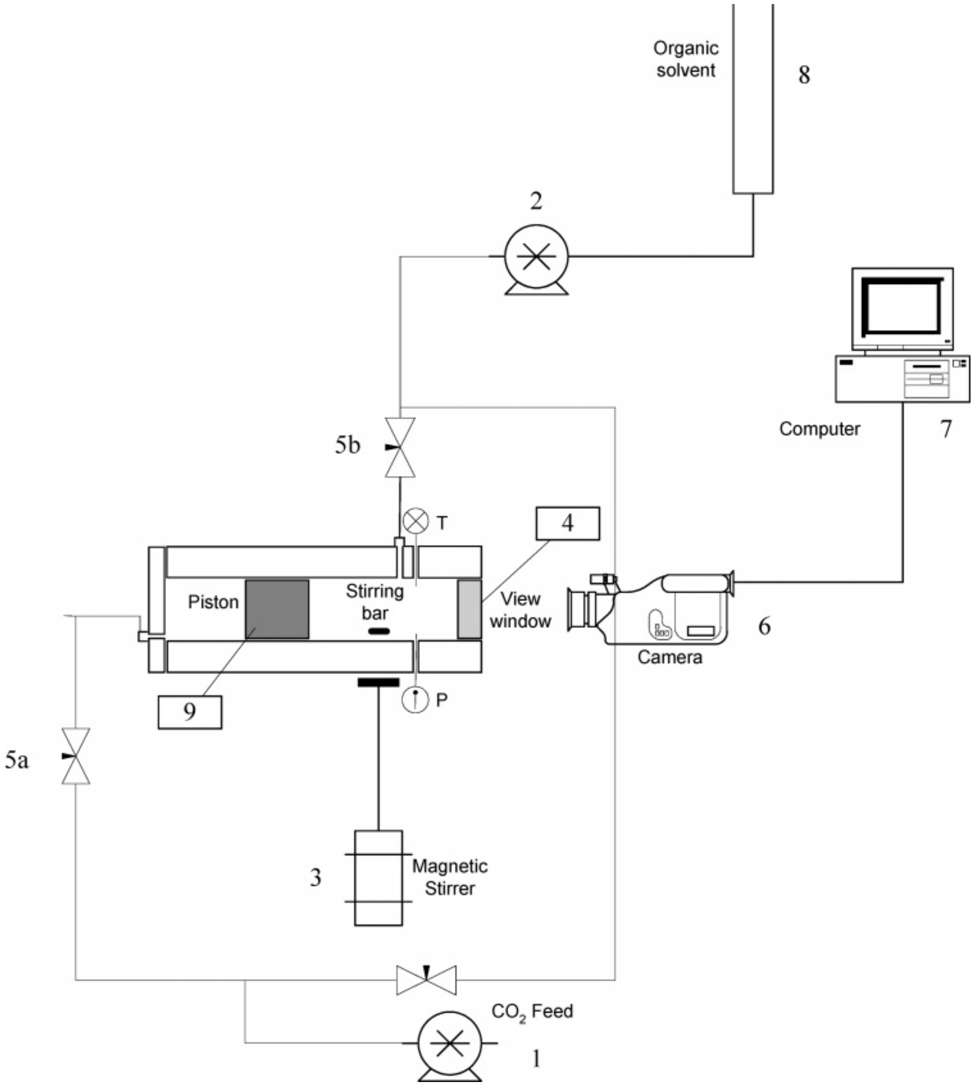

Figure 1. Schematic diagram of the experimental apparatus used for measuring bubble and cloud points.

Precise knowledge of the pressure and temperature of CO_2, with uncertainties of 0.05 bar and 0.05 K, respectively, allows for the calculation of its density with the recommended IUPAC equation of state.[10] As already mentioned, the volume of the cell and the dead volumes of the pressure gauge, the tubing, and the magnetic bar have been determined. Therefore, assuming that the amount of CO_2 dissolved in the polymer is negligibly small, the exact load and mass fraction of CO_2 can be calculated and controlled. Afterward, with a Milton Roy HPLC pump (2), dichloromethane is added to the cell via the same valve (5b) after the CO_2 feed is disconnected. The exact volume of the inserted dichloromethane is measured with a calibrated pipet placed at the inlet of the pump (8). In this way, the inserted amounts of all three components may be controlled, allowing for the precise control of the composition of the mixture and for reproducibility. As already mentioned, the pressure of the system is measured directly with the pressure gauge on the solvent side.

The cell is heated to the desired temperature with a silicon heating tape wrapped around it and insulated to ensure temperature stability. A Milton Roy pump feeds CO_2 through valve 5a causing the piston (9) to move, thus compressing the mixture. The magnetic stirrer agitates the mixture to ensure homogeneity. Once the state of a single phase is reached, the pressure is slowly released until a bubble or a cloud is formed. The mixture is compressed once again until the state of a single phase throughout is reached and the pressure is released once again. This is done several times, and the mixture is finally brought back to the state of a single phase and the pressure is slowly released. The relief rate is low, 1 bar/min, for the temperature to remain constant. Depending on the conditions, either a bubble is formed or a cloud, corresponding to L−V and L−L transitions, respectively. The pressures measured in each case are the pressure at which the first bubble is formed and the pressure at which the magnetic bar is no longer visible.[11] The temperature of the system was increased in 5 K increments to a maximum of 373.15 K for each mixture.

Results and Discussion

To test our experimental apparatus and procedure for validity and accuracy, a series of experiments were run. The mixture of CO_2 and dichloromethane was chosen for two reasons: it involves two of the components of the mixture to be studied, and more importantly, it has been thoroughly studied previously as a two-component system.[12] Our experimental data for the system $CO_2 + CH_2Cl_2$ with the variable-volume view cell are compared in Figure 2 with literature data.[12] The measurements were conducted at 308.15, 318.15, and 328.15 K and for various initial CO_2/CH_2Cl_2 loadings.

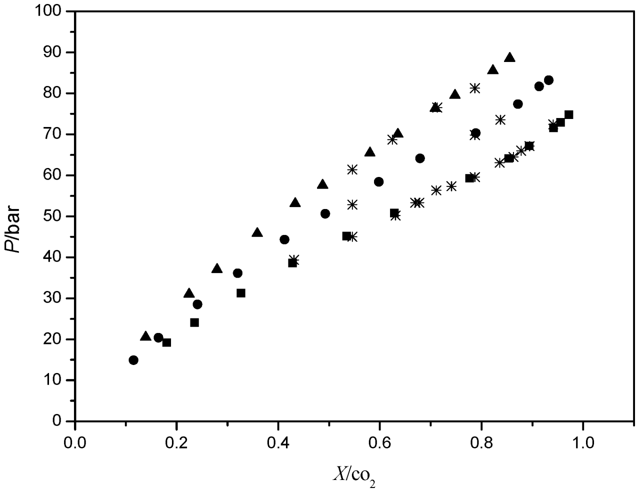

Figure 2. Bubble points for the mixture of dichloromethane + CO_2. Experimental data from this work are shown by stars. All other data are from ref 12 and correspond to the following: ●, 308.15 K; □, 313.15 K; ■, 318.15 K.

The agreement between the two sets of data is quite satisfactory, proving the precision and validity of our experimental apparatus and procedure.

Our interest, however, was in the phase-transition behavior of the ternary PLA + CO_2 + dichloromethane system. The type of phase transition along with the range of conditions where this system is a single phase are most important in the processes of micronisation or encapsulation of drugs in PLA. Special attention is given to the transitions that occur because they may be either L−V or L−L depending on the type of polymer, the solvent composition, and the temperature. Following the procedure described in the previous paragraph, we obtained the experimental data for the cloud and bubble points of our ternary system, which are reported in Table 1.

Three different PLA compositions were investigated for temperatures ranging from 308.15 to 373.15 K and pressures up to 240 bar. In Figures 3 to 5, the $P-T$ isopleths are shown for 0.01, 0.02, and 0.03 mass fractions of L-PLA, respectively.

Each curve corresponds to a specific CO_2-to-dichloromethane ratio. Depending on the conditions of temperature and solvent composition, the $P-T$ curves may have one or two different slopes. In the low-temperature region, an 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 an 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 is dependent on the PLA mass fraction and the CO_2/CH_2Cl_2 loadings. The higher the CO_2/CH_2Cl_2 mass ratio, the lower the temperature at which the L−L transition is first observed. Additionally, at L−V transitions, an increase in temperature leads to a correspondingly small increase of the bubble point. In L−L transitions, however, the temperature increase has a significant effect on the cloud point, increasing it dramatically. Being polar, dichloromethane is a good solvent for PLA, whereas CO_2 is not. A decrease in dichloromethane composition causes a corresponding decrease in solvent polarity, and thus, the solvent power of the mixture is decreased. CO_2, after all, is used as an antisolvent in processes where microparticles of PLA are produced.

Table 1. Experimental Data of Bubble and Cloud Points of PLA (1) in CH_2CL_2 (2) and CO_2 (3)[a,b]

$w_1 = 1\%$

	w_2 0.253 w_3 0.747	w_2 0.3442 w_3 0.6558	w_2 0.4003 w_3 0.5997	w_2 0.4491 w_3 0.5509	w_2 0.4776 w_3 0.5224	w_2 0.5148 w_3 0.4853
T/K	P/bar	P/bar	P/bar	P/bar	P/bar	P/bar
308.15	**34.12**	**41.55**	**42.35**	**49.08**	**49.96**	76.06
313.15	**37.24**	**45.16**	**46.06**	**53.39**	**54.5**	100.7
318.15	**40.05**	**49.18**	**49.86**	**58.2**	**59**	122.6
323.15	**43.06**	**52.69**	**53.69**	**63.73**	77.77	145.4
328.15	**45.87**	**56.6**	**57.7**	86.2	101.5	167.9
333.15	**49.28**	**60.62**	**62.12**	106.3	123.3	188.8
338.15	**52.59**	**65.03**	**66.63**	127.9	144.4	
343.15	**56.03**	**69.15**	**70.95**	147.7	164.7	
348.15	**59.41**	**73.36**	**75.36**	167.8	184.4	
353.15	**62.82**	**77.58**	**79.88**	186.1		
358.15	**66.24**	**82.19**	**84.29**			
363.15	**69.95**	**86.8**	97.14			
368.15	**73.43**	101	113.4			
373.15	**77.17**	117.4	130.4			

$w_1 = 2\%$

	w_2 0.2527 w_3 0.7473	w_2 0.344 w_3 0.656	w_2 0.4004 w_3 0.5996	w_2 0.446 w_3 0.554	w_2 0.4783 w_3 0.5217	w_2 0.5175 w_3 0.4825
T/K	P/bar	P/bar	P/bar	P/bar	P/bar	P/bar
308.15	**34.53**	**41.85**	**45.46**	**49.68**	**54.59**	93.42
313.15	**37.34**	**45.46**	**49.47**	**54.3**	**63.42**	120.7
318.15	**40.25**	**49.28**	**53.69**	**59.21**	85.9	144.2
323.15	**43.26**	**53.19**	**58.1**	70.05	108.4	167.1
328.15	**46.37**	**57.11**	**62.62**	92.53	130	190
333.15	**49.68**	**61.22**	**67.23**	113.6	150.8	211.6
338.15	**52.99**	**65.44**	**71.85**	133.7	171.3	233.2
343.15	**56.3**	**69.85**	**78.17**	154.6	190.9	
348.15	**59.91**	**74.26**	97.64	174.9	209.9	
353.15	**63.22**	**78.58**	116.3		228.9	
358.15	**66.94**	**83.09**	134.9			
363.15	**70.45**	**88.71**	152.9			
368.15	**73.96**	106.1	170.2			
373.15	**77.67**	122.3	187			

$w_1 = 3\%$

	w_2 0.2525 w_3 0.7475	w_2 0.3432 w_3 0.6568	w_2 0.4004 w_3 0.5996	w_2 0.4399 w_3 0.5601	w_2 0.4778 w_3 0.5222	w_2 0.517 w_3 0.483
T/K	P/bar	P/bar	P/bar	P/bar	P/bar	P/bar
308.15	**34.63**	**42.05**	**46.87**	**50.78**	59.81	106.8
313.15	**37.44**	**45.96**	**50.98**	**55.5**	82.79	129.5
318.15	**40.45**	**49.78**	**55.4**	**63.53**	105.9	153.7
323.15	**43.36**	**53.59**	**59.91**	86.5	129.7	175.8
328.15	**46.47**	**57.6**	**64.33**	108.3	151.6	198
333.15	**49.78**	**61.82**	**69.35**	129.4	173.1	219.8
338.15	**53.09**	**66.23**	81.89	150.9	194.5	240.6
343.15	**56.6**	**70.65**	101.7	171.2	214.5	
348.15	**60.22**	**75.16**	121.1	191.2		
353.15	**63.73**	**79.58**	139.6			
358.15	**67.34**	**84.09**	158.2			
363.15	**70.85**	96.03	175.9			
368.15	**74.56**	113.4				
373.15	**78.08**	129.9				

[a] w_1, w_2 and w_3 are mass fractions; w_2 and w_3 are calculated on a polymer-free basis. [b] Bold data are L−V transitions; the rest are cloud points.

The above observations are characteristic of the LCST behavior of polymer−solvent−gas systems described by Bungert et al.[13] The increase in temperature results in the expansion of the CH_2Cl_2 as it approaches its critical point. The polymer, being away from its critical point, does not expand significantly, and this creates a difference in the "free volume" contribution that eventually leads to a liquid−liquid phase separation. Moreover, the presence of the CO_2, which acts as an antisolvent, amounts to an increase in the free volume difference as that caused by a temperature increase. As a result, the L−L transition is shifted to lower temperatures with increasing amounts of CO_2. Thus, the LCST behavior of the system can be

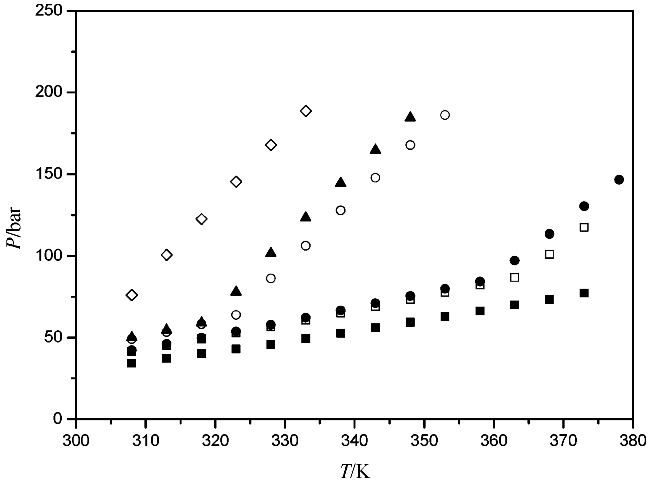

Figure 3. $P-T$ isopleths of cloud points of mass fraction L-PLA = 1% in dichloromethane + CO_2. Mass fractions of CO_2 in the mixed solvent on a polymer-free basis: ■, 0.253; □, 0.3442; ●, 0.4003; ○, 0.4491; ▲, 0.4776; ◇, 0.5148.

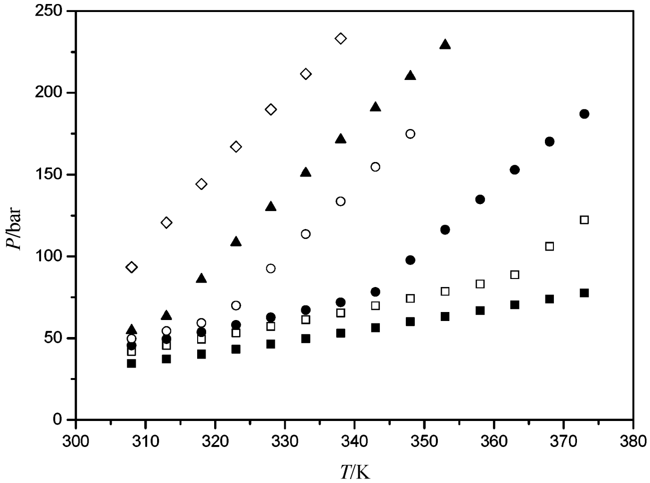

Figure 4. $P-T$ isopleths of cloud points of mass fraction L-PLA = 2% in dichloromethane + CO_2. Mass fractions of CO_2 in the mixed solvent on a polymer-free basis: ■, 0.2527; □, 0.344; ●, 0.4004; ○, 0.446; ▲, 0.4783; ◇, 0.5175.

manipulated in a way that is beneficial to the micronisation process.

The effect of the dichloromethane mass fraction is better followed with the aid of Figure 6. For a polymer mass fraction of 3%, the effect of the CO_2/CH_2Cl_2 loading is clearly shown in this Figure.

Moreover, a 3-D diagram is presented in Figure 7, where the effect of both temperature and CO_2 composition is shown for a polymer mass fraction of 3%.

Lee et al.[8] studied the same system for different molecular weights of PLA, which are significantly lower than ours. The effects of temperature, solvent composition, and molecular weight of the polymer on the L−L transitions were investigated. The polymer mass fraction for these studies was fixed at 5%. In Table 2 are presented the data of Lee et al.[8] along with our data for the same solvent composition but for the PLA of M_w 189 000.

Lee et al.[8] suggested that an increase in molecular weight leads to a corresponding increase in the cloud point pressure This was confirmed by our own studies for the different CO_2/CH_2Cl_2 mass ratios. This observation also agrees with the LCST behavior mentioned earlier; that is, an increase in M_w leads to lower temperatures and higher pressures according to Bungert et al.[13] All L−L transitions occurred at higher pressures with PLA of M_w 189 000. Additionally, for CO_2-rich systems, the slope of the cloud points with temperature and M_w is steeper compared to that of systems with the same PLA mass fraction that are richer in CH_2Cl_2, in agreement with the observations of

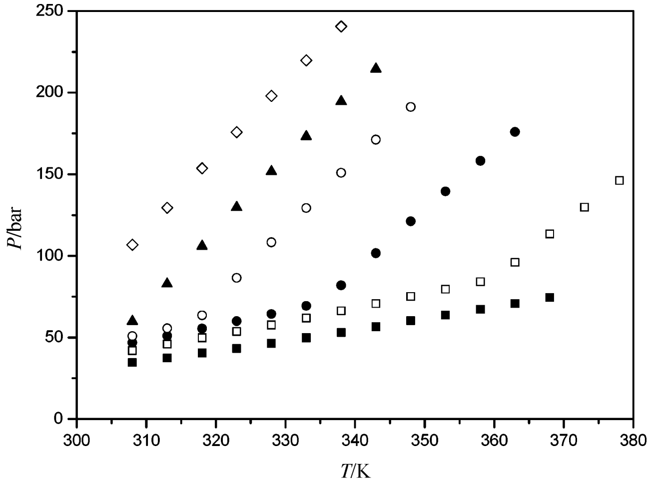

Figure 5. $P-T$ isopleths of cloud points of mass fraction L-PLA = 3% in dichloromethane + CO_2. Mass fractions of CO_2 in the mixed solvent on a polymer-free basis: ■, 0.2525; □, 0.3432; ●, 0.4004; ○, 0.4399; ▲, 0.4778; ◇, 0.517.

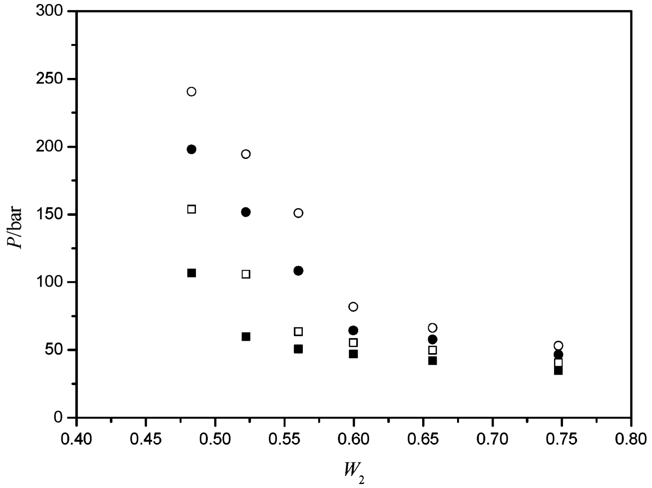

Figure 6. Effect of dichloromethane composition w_2 in a mixed solvent on bubble and cloud point pressures of L-PLA (mass fraction = 3%) at various temperatures: ■, 308.15; □, 318.15; ●, 328.15; ○, 338.15.

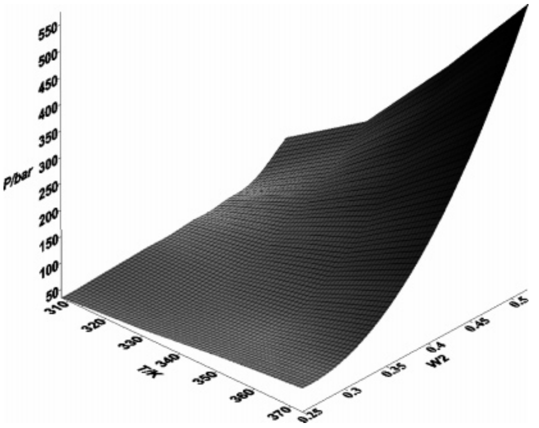

Figure 7. Cloud points of PLA in the dichloromethane + CO_2 (w_2) solvent mixture, in $P-T-X_{CO_2}$ space. The PLA mass fraction is 3%.

Table 2. Experimental Data of Cloud Points of PLA (1) in CH_2Cl_2 (2) and CO_2 (3)[a]

	T/K	P^b/bar	P/bar
		M_w 50 000	M_w 189 000
w_1	312.35	**52.6**	**53.8**
(mass fraction)	322.35	**61.4**	75.06
0.0508	333.55	86.7	123.93
w_2	342.45	122.9	160.25
0.5356	353.15	162.3	200.29
		M_w 50 000	M_w 189 000
w_1	311.65	**48.2**	**49.1**
(mass fraction)	322.75	**57.5**	**58.5**
0.0509	332.45	**67.6**	**68.7**
	345.05	79.7	98.3
w_2	352.35	107.3	125.4
0.5928	361.75	135.5	159.4
	373.15	174.3	199
		M_w 100 000	M_w 189 000
w_1	314.35	**54.5**	101.85
(mass fraction)	322.85	73.7	141.49
0.0513	333.15	117.2	186.54
	343.55	159.4	231.6
w_2			
0.5162			

[a] Bold data are L−V transitions; the rest are cloud points. The mass fraction of CH_2Cl_2 is calculated on a polymer-free basis. [b] P^{**} are the data of Lee et al.[8]

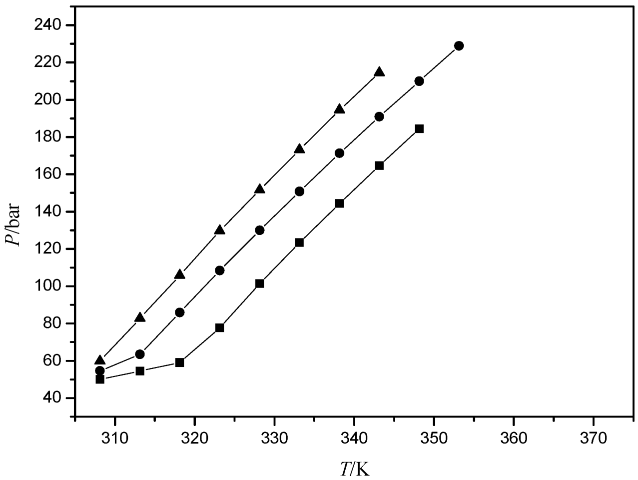

Figure 8. Effect of PLA composition in a mixed solvent of CO_2 (mass fraction = 0.4776 on a polymer-free basis) and dichloromethane (mass fraction = 0.5224 on a polymer-free basis). Mass fraction of PLA: ■, 1%; ●, 2%; ▲, 3%.

Lee et al.[8] The versatility of our experimental technique allowed for additional observations. In particular, it was observed that an increase in M_w leads to a corresponding increase in the bubble points for specific PLA mass fractions and CO_2/CH_2Cl_2 ratios.

A very important factor, which was not considered by Lee et al.,[8] is the polymer concentration. When comparing Figures 3 to 5 for the same temperature and solvent composition, it is observed that the bubble point also depends on the polymer concentration. The higher the polymer concentration, the higher the pressure at which the L−V or L−L transitions occur for a given temperature and solvent composition. Figures 8 and 9 show the effect of this factor on the L−V and L−L transitions

It is obvious that the greater the polymer concentration, the greater the pressure necessary to maintain the mixture in the single phase for a standard CO_2/CH_2Cl_2 loading. Moreover, as the polymer concentration increases, the change from L−V to L−L transitions is shifted to lower temperatures, an observation that is very important when it comes to the choice of the values of the parameters involved in the process of micronisation. A comparison of Figures 8 and 9 in the low-temperature region shows the effect that PLA concentration has on the bubble points. In the case of Figure 9, the increase in PLA concentration at low temperatures leads to a slight increase in the pressure needed to maintain the single phase. This increase is larger in the case of Figure 8. The explanation for this is the different CO_2/CH_2Cl_2 loadings in each case. The greater the CO_2 concentration, the greater the impact the PLA mass fraction has on the bubble points. Specifically, in the case of minimum CO_2 mass fraction on a polymer-free basis (0.2525), an increase in PLA mass fraction equal to 1 to 2% results in a 0.3 bar increase in the bubble point at 308.15 K, whereas in the case of maximum CO_2 mass fraction (0.5175) an increase in PLA mass fraction equal to 1 to 2% results in a 4.6 bar increase in the bubble point. It is worth mentioning that this observation is in apparent contradiction with the corresponding observation of Lee et al.[8] that the L−V transitions occur on the bubble line of the dichloromethane + CO_2 system. This may be the case for polymers of low M_w, but in the case of high molecular weights, the PLA mass fraction has a noticeable effect on the L−V transitions.

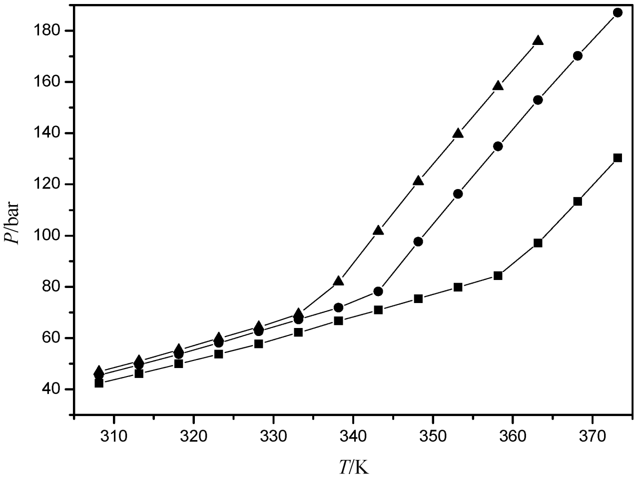

Figure 9. Effect of PLA composition in a mixed solvent of CO_2 (mass fraction = 0.4003 on a polymer-free basis) and dichloromethane (mass fraction = 0.5997 on a polymer-free basis). Mass fraction of PLA: ■, 1%; ●, 2%; ▲, 3%.

Conclusions

The experimental setup and procedure of this work allows for reliable control of all process parameters, which in turn leads to reproducible results. With this setup, the bubble and cloud points were determined for the ternary system PLA + CO_2 + dichloromethane. Depending on the temperature, the polymer concentration, and the CO_2/CH_2Cl_2 mass ratio, L−V or L−L 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. Systems with specific CO_2/CH_2Cl_2 mass ratios and for a mass fraction equal to 0.05 in PLA of M_w 189 000 were reproduced and compared with the corresponding experiments of Lee et al.[8] The effect of molecular weight on the L−L transitions observed by Lee et al. was confirmed by our study, and a similar effect was observed for the L−V transitions as well. Moreover, the shift of L−L transitions to lower temperatures with the increase of M_w and the depression of L−V transitions was also noticed.

An increase in dichloromethane concentration caused an increase in the polarity of the solvent, leading to a shift of the L−V and L−L transitions to higher temperatures and lower pressures. Moreover, the LCST behavior of the system was observed, and the effects of the CO_2 addition and temperature increase were investigated with respect to this behavior.

Finally, the effect of the polymer concentration was investigated. An increase in the polymer mass fraction led to an increase in the bubble and cloud point pressures. In the case of the bubble points, the observed increase in bubble pressure was more significant in systems rich in CO_2, and it was always above the bubble point line of the binary dichloromethane + CO_2 system.

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