

Phase Equilibria of Poly(methyl methacrylate) in Supercritical Mixtures of Carbon Dioxide and Chlorodifluoromethane

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(Received 22 May 2001 • accepted 2 July 2001)

Abstract—Phase behavior data are presented for poly(methyl methacrylate) (PMMA; $M_w = 15,000, 120,000$) in supercritical solvent mixtures of carbon dioxide (CO_2) and chlorodifluoromethane (HCFC-22). Experimental cloud point curves, which were the phase boundaries between single and liquid-liquid phases, were measured by using a high-pressure equilibrium apparatus equipped with a variable-volume view cell at various CO_2 compositions up to about 63 wt% (on a polymer-free basis) and at temperatures up to about 100 °C. The cloud point curves exhibited the characteristics of a lower critical solution temperature phase behavior. As the CO_2 content in the solvent mixture increased, the cloud point pressure at a fixed temperature increased significantly. Addition of CO_2 to HCFC-22 caused a lowering of the dissolving power of the mixed solvent due to the decrease of the solvent polarity. The cloud point pressure increased with increasing the molecular weight of PMMA.

Key words: Poly(methyl methacrylate), Carbon Dioxide (CO_2), Chlorodifluoromethane (HCFC-22), Cloud Point, Supercritical

INTRODUCTION

Supercritical fluids (SCFs) have been used as solvents in a variety of chemical processes such as extractions and separations, fractionations, and reactions [McHugh and Krukoni, 1994; Chang et al., 1996; Ryu and Kim, 1996; Noh et al., 1997]. Particularly, SCF technology has recently gained great attention in the particle formation of polymers [Bodmier et al., 1995; Reverchon et al., 2000]. SCF solvents are an attractive alternative to incompressible organic liquid solvents, since they can have liquid-like dissolving power while exhibiting transport properties of a gas. Phase behavior data for polymer-SCF systems are required for efficient operation and design of SCF polymer processes.

The selection of SCF solvents to dissolve polymers is often challenging for processing applications because it is difficult to find a good SCF solvent that will dissolve the polymer at relatively moderate conditions. Carbon dioxide (CO_2) is the favorite solvent in SCF processes because it has a relatively low critical temperature and pressure and because it is inexpensive, nonflammable, nontoxic, and readily available. However, it is generally not a good solvent for dissolving high molecular weight polymers with the exception of fluoro-polymers [Mawson et al., 1995] and siloxane polymers [Xiong and Kiran, 1995]. Thus it has been used as an antisolvent when forming polymer particles using the SCF processes such as a supercritical antisolvent precipitation method [Reverchon, 1999]. On the other hand, chlorodifluoromethane (HCFC-22) has been known to be a good solvent for polar polymers [Meilchen et al., 1991; Haschets and Shine, 1993].

The physical properties of the solvents studied in this work are shown in Table 1, where μ is the permanent dipole moment and α is the polarizability. HCFC-22 and CO_2 are highly volatile and nontoxic, and have relatively lower critical temperatures than organic

liquid solvents. A solvent will dissolve a polymer if it can interact favorably with the polymer through intermolecular forces, such as hydrogen bonding and dipole-dipole interactions. The specific choice of SCF solvents for a given polymer is highly dependent on the intermolecular forces between solvent-solvent, solvent-polymer, and polymer-polymer pairs in solution. As shown in Table 1, HCFC-22 is a polar solvent with high dipole moment and polarizability. It can form hydrogen bonding with base molecules but it does not form self-association [McHugh and Krukoni, 1994]. Therefore, its polar dipole moment is expected to interact favorably with that of a polar polymer. However, CO_2 is a nonpolar solvent with no dipole moment.

Because poly(methyl methacrylate) (PMMA) is a very polar polymer, it does not dissolve in nonpolar solvents such as n-hexane and supercritical CO_2 , or in moderately polar solvents such as toluene. PMMA does dissolve in HCFC-22, chloroform, and dichloromethane even at room temperature because all of them have large dipole moments and are capable of donating a hydrogen to the basic acrylate group on the polymer. Even low molecular weight PMMA of 50,000 does not dissolve in CO_2 or ethylene at 700 bar and 150 °C even though both of these solvents have quadrupole moments and CO_2 has some acid-base character. It is reported that PMMA in hundreds of thousands molecular weight range readily dissolves to 20 wt% in HCFC-22 at a modest temperature of 120 °C and pressures of 200-300 bar [McHugh and Krukoni, 1994]. HCFC-22 is a very polar hydrogen-donor solvent that is capable of hydrogen bonding to the basic acrylate group in the backbone of PMMA. Several other studies [Meilchen et al., 1991; Haschets and Shine, 1993; Lele and Shine, 1994; Lee et al., 2000] have also shown that HCFC-22 is an excellent solvent for polar polymers that can cross-associate with the acidic hydrogen in this solvent.

Consequently, CO_2 is a poor solvent for PMMA, while HCFC-22 is an excellent solvent for the same polymer. The addition of polar HCFC-22 to CO_2 provides enhanced polar interactions between PMMA and the mixed solvent that are expected to lead to in-

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Table 1. Physical properties of the solvents used in this study*

Name	Formula	M.W.	T _c (°C)	P _c (bar)	μ (debye)	α (Å ³)
Chlorodifluoromethane (HCFC-22)	CHClF ₂	86.469	96.15	49.90	1.458	6.38
Carbon dioxide	CO ₂	44.01	31.06	73.84	0.0	2.911

*T_c, P_c, μ are obtained from the REFPROP database [McLinden et al., 1998], and α from the CRC handbook [Lide, 1995].

creased solubility. Thus, one can adjust the dissolving power of the solvent for PMMA by utilizing a mixture of CO₂ and HCFC-22 as an SCF solvent. This work is focused on determining the feasibility of dissolving PMMA in CO₂+HCFC-22 solvent mixtures. We present the phase behavior data for the PMMA polymer in supercritical mixtures of CO₂ and HCFC-22. The cloud point pressures were measured by using a high-pressure variable-volume view cell apparatus and were characterized as functions of CO₂ composition in the solvent mixture and polymer molecular weight. The phase behavior data produced in this work would be useful for establishing operating conditions in the particle formation of PMMA by the supercritical antisolvent precipitation process that utilizes HCFC-22 as a solvent and CO₂ as an antisolvent.

EXPERIMENTAL

1. Materials

PMMA's were purchased from Aldrich Chemical Co. (Milwaukee, WI, USA) and used without further purification. They have the weight average molecular weights (M_w) of 15,000 and 120,000 g/mol, respectively, provided by the supplier. CO₂ and HCFC-22 were obtained from Myung-Sin General Gas Co. (Yangsan, Kyungnam, Korea) and Solvay Fluorides Inc. (Greenwich, CT, USA), respectively, and their certified purities were 99.99 wt%. They were used as received without further purification.

2. Apparatus

Fig. 1 shows a schematic diagram of the experimental apparatus for measuring the cloud point behavior of a polymer in a high-pres-

sure solvent. The experimental apparatus is similar to that used by Lee et al. [2000]. The heart of the system is the high-pressure variable-volume view cell. The cell has dimensions of 16 mm i.d. by 70 mm o.d., and an internal working volume of about 31 cm³. A movable piston is placed inside the cell to change the cell volume. A pressure generator (High Pressure Equipment Co. model 50-6-15) is used to pressurize water and therefrom displace the piston. A change in the cell volume causes a change of the system pressure. A sapphire window (3/4" diameter by 3/4" thick) is inserted into the view cell for visual observation of the interior of the cell. A main feature of using the variable-volume cell apparatus is that the concentration of the system is kept constant during the experiment. On the other side, using a constant-volume cell apparatus often requires venting off solution to decrease the pressure of the system, causing unknown changes in the concentration of the cell contents.

The system pressure is measured with a high-precision pressure gauge (Dresser Heise model CC-12-G-A-02B, 1,000 bar max. pressure, ±1.0 bar accuracy) installed on the pressurizing fluid (water) side between the pressure generator and the cell. Connecting the pressure gauge directly to the solvent side of the cell can cause an uncertainty in the exact concentration of the solution due to dead volume and can plug the line due to high viscosity in the case of a high polymer concentration solution. The pressure drop was observed to be about 0.5 bar across the piston, and thus in each experiment the cloud point pressure was increased by 0.5 bar to account for the pressure drop. The system temperature is measured to within ±0.1 °C by an RTD (Pt-100Ω) probe inserted into the cell. An oil bath is used to keep the system temperature constant, and

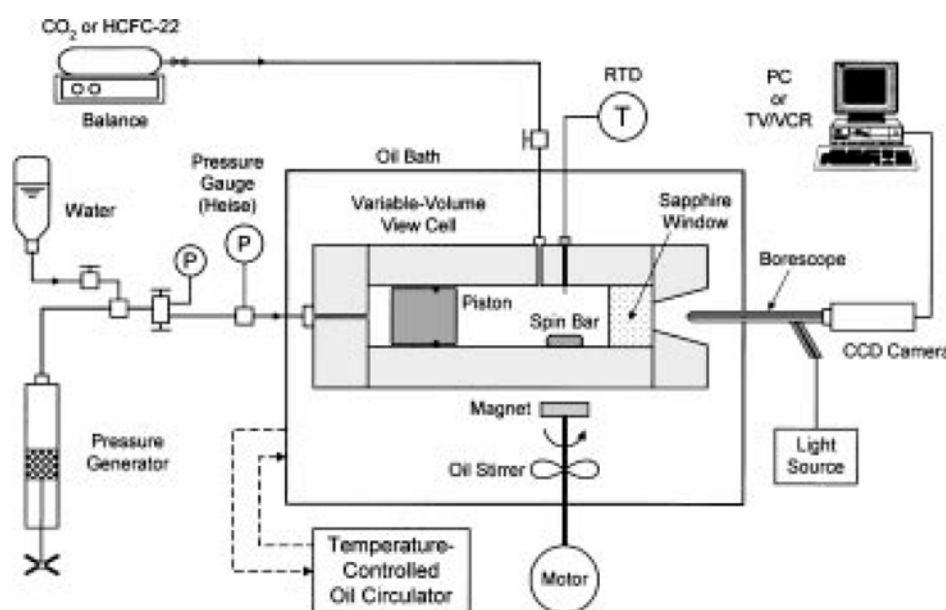


Fig. 1. A schematic diagram of the experimental apparatus for measuring cloud points.

its temperature is controlled by an oil circulator (Jeio-Tech model HTC-30D).

A visual observation of the cell inside through the sapphire window is made by a borescope (Olympus model R080-044-000-50) and a CCD camera (WAT-202B) connected to a TV/VCR monitor and a computer. A cold light source (Olympus model ILK-5) is used to provide illumination inside the view cell. A magnetic stirring system is equipped under the cell body to agitate the polymer solution. A stirring bar in the cell is rotated by a samarium-cobalt magnet located below the cell, and the magnet is driven by an electric motor and an RPM controller.

3. Method

The experiment for measuring the cloud point of PMMA in a mixture of HCFC-22 and CO₂ was performed by the following procedure. To remove any entrapped air present in the cell, the cell was purged with enough amount of CO₂ gas. A certain amount of the PMMA polymer was loaded into the cell, and then the stirring bar was placed inside the cell. The amount of the polymer loaded into the cell was determined by using a sensitive balance (AND model HM-300) measurable to ± 0.1 mg. After a piston and o-rings into the view cell were assembled, the cell was placed inside the oil bath. The solvent was charged into the cell using a high-pressure sample cylinder. In case of charging both HCFC-22 and CO₂, HCFC-22 was first charged because its vapor pressure was lower than that of CO₂. The composition of each component in the solvent mixture was determined by weighing HCFC-22 and CO₂ sample cylinders before and after charging them into the cell using a balance (Precisa model 1212 M SCS) with an accuracy of ± 1 mg.

The solution in the cell was compressed by moving the piston located within the cell using the pressure generator. As the pressure generator pressurizes water, the compressed water displaces the piston to the window side to decrease the cell volume and thus raise the pressure in the cell. As the pressure increases, the solution in the cell finally becomes a single homogeneous phase. At the same time the solution was well agitated by a stirring bar.

The system was heated to a desired temperature. Once the system reached thermal equilibrium and the solution was maintained at a single phase, the pressure was then slowly reduced until the solution became cloudy, by displacing the piston back to the water side with the pressure generator. Enough time was allowed to ensure thermal equilibrium during the pressure reduction. The pressure was reduced at a rate of about 0.5 bar/min when the cloud point pressure was approached. At a fixed polymer concentration, solvent composition, and temperature, the cloud point indicating the single to liquid-liquid phase transition was defined as the pressure at which it was no longer possible to visually observe the stirring bar [Meilchen et al., 1991; Lee et al., 2000]. For obtaining consistent measurements, every measurement was repeated at least twice at each temperature.

The temperature of the system was raised in about 10 °C increments, and the above procedure was repeated, thus creating a pressure-temperature (P-T) cloud point curve at fixed polymer and solvent concentrations. In this work the PMMA concentration was kept constant arbitrarily around 5 wt% in order to exclude the effect of the polymer concentration on the phase behavior. The maximum temperature was set to about 100 °C to avoid thermal degradation of o-rings and polymers.

RESULTS AND DISCUSSION

The phase behavior of PMMA in a mixed solvent of CO₂ and HCFC-22 was investigated as a function of temperature, polymer

Table 2. Experimental data of cloud points of PMMA ($M_w=15,000$) in solvent mixtures of CO₂ and HCFC-22

CO ₂ composition in mixed solvent* (wt%)	PMMA concentration in solution** (wt%)	Temperature (°C)	Pressure (bar)		
0.00	4.98	59.2	24.5***		
		64.5	29.6		
		69.7	45.5		
		80.0	77.9		
		90.2	108.5		
		99.8	138.7		
		12.48	5.03	29.7	21.5***
12.48	5.03	37.4	24.8***		
		50.1	37.5		
		59.6	74.5		
		69.5	111.5		
		79.8	146.2		
		89.7	180.6		
		99.6	213.0		
		18.09	5.00	40.4	32.5***
		18.09	5.00	49.5	63.7
				59.8	104.7
69.7	143.2				
79.5	178.5				
89.8	216.0				
100.0	250.9				
30.74	4.91			29.6	33.7***
30.74	4.91			39.6	96.5
				49.4	145.5
				59.8	192.7
		69.5	231.4		
		79.7	275.5		
		89.7	314.4		
		99.8	351.5		
		37.67	4.99	27.6	35.5***
		37.67	4.99	40.1	152.7
				50.0	204.5
60.0	253.5				
69.9	294.3				
79.9	338.0				
89.9	379.5				
99.9	417.0				
44.98	4.99			30.2	40.6***
44.98	4.99			39.9	225.5
				49.6	278.3
		59.5	331.1		
		70.1	378.5		
		79.4	420.5		
		89.5	459.5		
		99.4	499.5		

Table 2. Continued

CO ₂ composition in mixed solvent* (wt%)	PMMA concentration in solution** (wt%)	Temperature (°C)	Pressure (bar)
52.22	4.98	37.3	50.9***
		39.9	319.0
		50.6	377.4
		60.1	432.5
		69.6	476.8
		79.2	520.5
		89.7	567.5
		99.5	604.5
62.97	5.09	39.9	550.5
		49.6	602.6
		59.5	654.9
		69.7	697.7
		79.5	742.3
		89.8	779.3
		100.0	816.2

*On a polymer-free basis.

**Weight percent of total in solution.

***Liquid to liquid-vapor transition pressure.

molecular weight, and solvent composition in mixed solvents. The experimental cloud point data are given in Tables 2 and 3. In this work, the polymer concentration in the solution was fixed at about 5 wt%, to eliminate the effect of the polymer concentration on the cloud points. For most of polymer-SCF systems, it is known that the polymer concentration of about 5 wt% is the concentration to give the maximum pressure in the pressure-polymer concentration isotherm [McHugh and Krukoni, 1994]. Haschets and Shine [1993] also reported that the maximum pressure was observed at the pol-

Table 3. Experimental data of cloud points of PMMA (M_w=120,000) in solvent mixtures of CO₂ and HCFC-22

CO ₂ composition in mixed solvent* (wt%)	PMMA concentration in solution** (wt%)	Temperature (°C)	Pressure (bar)
0.00	4.99	39.6	16.6***
		50.3	21.6***
		52.6	24.7
		59.7	49.5
		69.1	85.1
		80.1	125.5
		89.4	159.2
		100.0	195.7
9.97	5.10	36.5	24.5***
		40.1	32.0
		49.4	71.7
		59.5	116.0
		68.7	154.5
		80.7	204.5
		89.2	238.5
		100.0	278.5

Table 3. Continued

CO ₂ composition in mixed solvent* (wt%)	PMMA concentration in solution** (wt%)	Temperature (°C)	Pressure (bar)
17.00	4.96	40.0	77.5
		49.8	123.7
		59.7	171.1
		69.5	215.9
		79.7	260.5
		88.8	297.5
		100.0	344.0
		21.44	5.02
50.8	168.4		
60.1	215.5		
69.6	260.7		
79.5	306.1		
89.7	352.4		
99.4	392.6		
29.50	4.92		
		49.5	242.5
		59.1	295.1
		69.3	349.0
		79.3	397.5
		89.2	445.5
		99.5	491.3
		39.17	4.91
49.3	366.6		
59.1	426.5		
70.7	492.0		
79.2	540.5		
89.5	591.0		
100.1	640.7		
47.26	5.23		
		49.7	525.5
		60.0	591.6
		69.5	649.5
		79.8	708.7
		89.2	756.1
		100.2	810.0
		53.59	4.88
50.3	719.7		
59.4	779.3		
69.6	840.5		
80.1	897.0		

*On a polymer-free basis.

**Weight percent of total in solution.

***Liquid to liquid-vapor transition pressure.

mer concentration between 3 and 8 wt% for the PMMA/HCFC-22 system.

Fig. 2 shows the P-T isopleths of the cloud points of PMMA in pure HCFC-22 solvent for the PMMAs with molecular weights of 15,000 and 120,000. The saturation curve of HCFC-22, which is obtained from Daubert and Danner [1994], is also shown along with the cloud point data. Above each cloud point is the single-phase

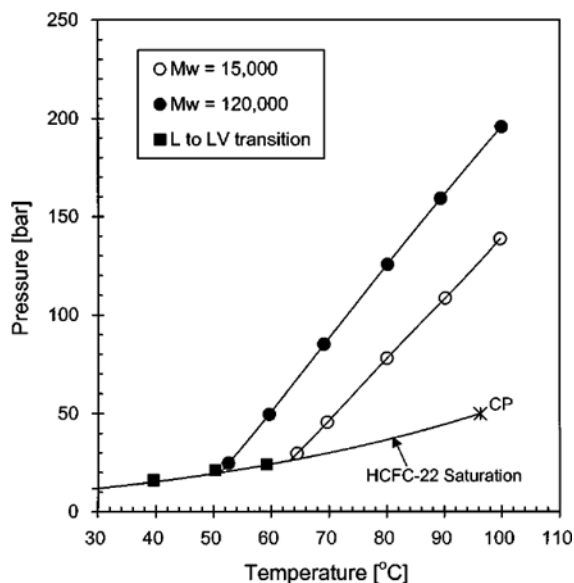


Fig. 2. Effect of polymer molecular weight on cloud points of PMMA in pure HCFC-22.

region, and below the point is the liquid-liquid two-phase region. The cloud point pressure increased as the temperature increased, indicating that the system exhibited a typical lower critical solution temperature (LCST) behavior. In other words, as the temperature increased, a higher pressure was needed to obtain a single-phase solution from a two-phase solution. The cloud point pressure was as low as about 200 bar even at 100 °C for the PMMA of $M_w=120,000$, indicating that HCFC-22 was an excellent solvent to dissolve the PMMA. HCFC-22 can form hydrogen bonding with the base molecules, and thus the enhanced solvent power of HCFC-22 is attributed to the hydrogen bonding of the hydrogen atom in HCFC-22 with the acrylate group in the backbone of PMMA. The effect of the hydrogen bonding is evident with the HCFC-22 cloud point curves, which are situated at very low pressures.

As the PMMA molecular weight increased, the cloud point pressure increased. Increasing the polymer molecular weight reduced the single-phase region. This indicates that PMMA becomes less soluble in HCFC-22 as its molecular weight increases, which is consistent with the results of other polymer-SCF systems. The cloud point curves intersected the HCFC-22 saturation curve at the lower critical end points (LCEPs), at which the fluid to liquid-liquid phase transition ended. The liquid to liquid-vapor phase transitions occurred on the HCFC-22 saturation curve at temperatures below the LCEP. As shown in Fig. 2, the liquid to liquid-vapor transition points measured experimentally agreed well with the HCFC-22 saturation curve. The LCEP was observed around 63 °C for the PMMA of $M_w=15,000$, and around 51 °C for the PMMA of $M_w=120,000$.

Fig. 3 shows the P-T isopleths of the cloud points of PMMA ($M_w=15,000$) in the mixed solvents of CO_2 and HCFC-22 for various CO_2 compositions up to about 63 wt% (on a polymer-free basis). The PMMA concentration in the solution was kept constant at (5.00 ± 0.03) wt% of total. For all the CO_2 compositions, the cloud point curves exhibited the characteristics of an LCST curve and had similar slopes. CO_2 is not a good solvent to dissolve the PMMA polymer. In our preliminary work PMMA ($M_w=15,000$) was observed

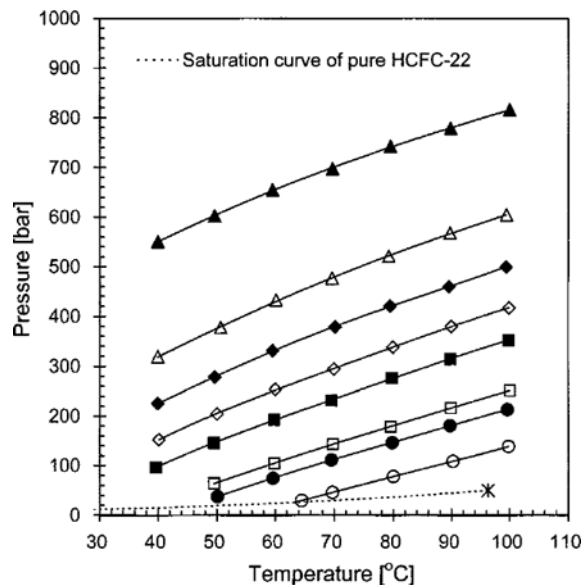


Fig. 3. P-T isopleths of cloud points of PMMA ($M_w=15,000$) in a CO_2 +HCFC-22 mixed solvent. Compositions of CO_2 in the mixed solvent on a polymer-free basis: (○) 0.0 wt%; (●) 12.48 wt%; (□) 18.09 wt%; (■) 30.74 wt%; (◇) 37.67 wt%; (◆) 44.98 wt%; (△) 52.22 wt%; (▲) 62.97 wt%.

to be not completely soluble in pure CO_2 at pressures as high as 1,000 bar and at temperatures up to 100 °C. On the other hand, the PMMA was readily soluble in HCFC-22 of saturated liquid state, as shown in Fig. 2 or 3. However, the cloud point pressure at a fixed temperature increased significantly with increasing CO_2 content in the solvent mixture. As the CO_2 composition in the solvent increased, the cloud point curve was shifted to higher pressures so that the single-phase region of polymer-solvent miscibility shrunk. Addition of CO_2 to HCFC-22 caused a lowering of the dissolving power of

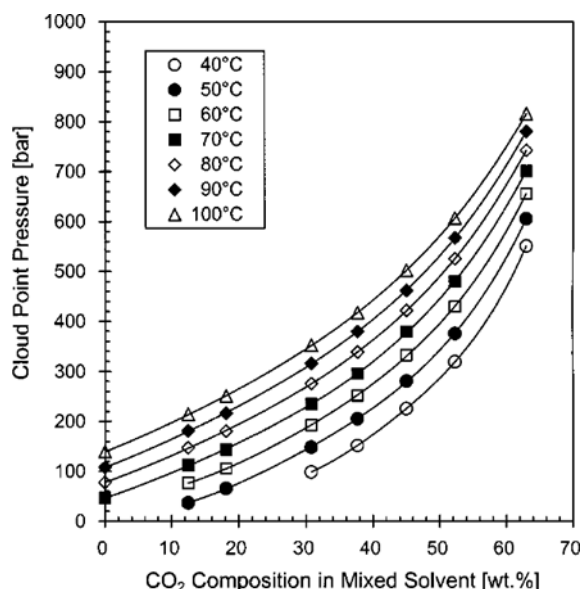


Fig. 4. Effect of CO_2 composition in a mixed solvent on the cloud point pressures of PMMA ($M_w=15,000$) at various temperatures.

the mixed solvent. This can be attributed to the decrease of the solvent polarity by the increase of CO₂ composition in the mixed solvent.

The P-T isopleths of the cloud points given in Fig. 3 were further characterized by drawing the cloud point pressures as a function of solvent composition. Fig. 4 shows the effect of CO₂ composition in the mixed solvent on the cloud point pressures at several temperatures for the PMMA ($M_w=15,000$). It was obtained by fitting the cloud point curves of Fig. 3 at different CO₂ compositions with polynomial equations and then by determining the pressures corresponding to desired temperatures from the curve fits. The correlation coefficients of the curve fits, which expressed the goodness of the fits, were greater than 0.999 for all cases. The cloud point pressures increased sharply with increasing the CO₂ composition in the mixed solvent.

Fig. 5 illustrates the P-T isopleths of the cloud points of PMMA ($M_w=120,000$) in the mixed solvents of CO₂ and HCFC-22 for various CO₂ compositions. The PMMA concentration in the solution was kept constant at (5.00 ± 0.09) wt% of total. Fig. 6 gives the effect of CO₂ composition in the mixed solvent on the cloud point pressures at several temperatures for the PMMA ($M_w=120,000$). Figs. 5 and 6 gave higher cloud point pressures than those in Figs. 3 and 4 because the PMMA of bigger molecular weight was used. As the CO₂ composition in the mixed solvent increased, the cloud point pressures increased sharply.

CONCLUSIONS

The phase behavior data were measured for the PMMA polymer in supercritical solvent mixtures of CO₂ and HCFC-22 by using a high-pressure equilibrium apparatus equipped with a variable-volume view cell. The cloud point pressures were determined as a

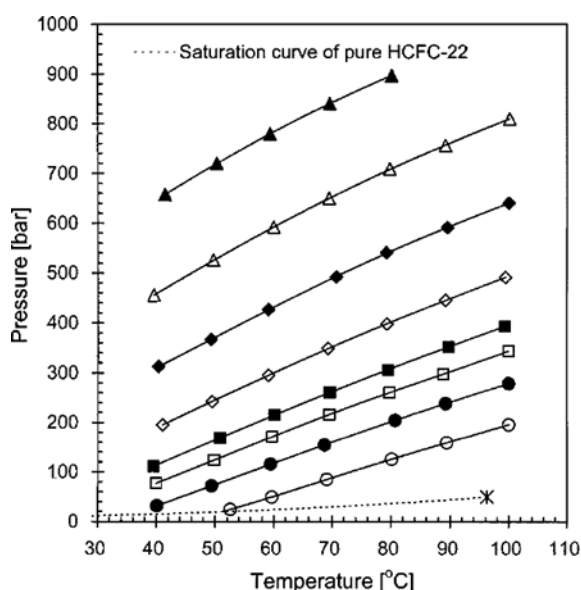


Fig. 5. P-T isopleths of cloud points of PMMA ($M_w=120,000$) in a CO₂+HCFC-22 mixed solvent. Compositions of CO₂ in the mixed solvent on a polymer-free basis: (○) 0.00 wt%; (●) 9.97 wt%; (□) 17.00 wt%; (■) 21.44 wt%; (◇) 29.50 wt%; (◆) 39.17 wt%; (△) 47.26 wt%; (▲) 53.59 wt%.

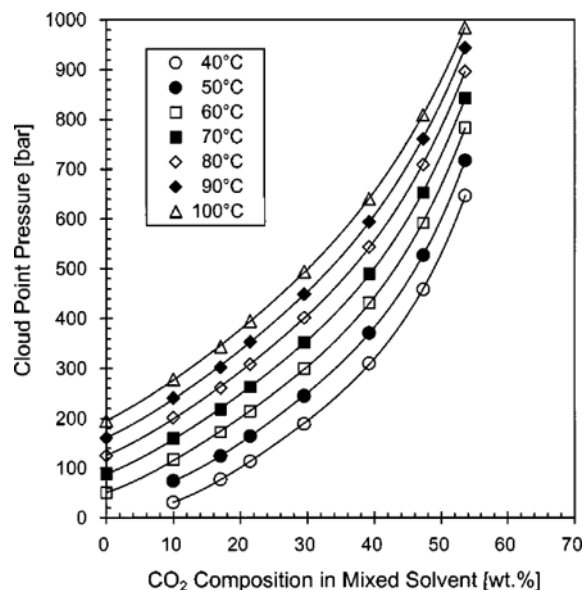


Fig. 6. Effect of CO₂ composition in a mixed solvent on the cloud point pressures of PMMA ($M_w=120,000$) at various temperatures.

function of solvent composition at various CO₂ compositions up to about 63 wt% (on a polymer-free basis) and at temperatures up to about 100 °C, and as a function of polymer molecular weight for the PMMAs with the molecular weights of 15,000 and 120,000. The cloud point curves exhibited the characteristics of an LCST-type phase behavior. As the CO₂ content in the solvent mixture increased, the cloud point pressure at a fixed temperature increased significantly. Addition of CO₂ to HCFC-22 caused a lowering of the dissolving power of the mixed solvent due to the decrease of the solvent polarity. The cloud point pressure increased with increasing the PMMA molecular weight.

ACKNOWLEDGMENT

This work was supported by a 2000 university research grant of Hannam University.

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