Phase Behavior of Poly(propylene glycol) Monobutyl Ethers in Dense CO_2

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An oxygenated hydrocarbon-based polymer, poly(propylene glycol) monobutyl ether (PPGMBE), is very CO_2-soluble. Therefore PPGMBE may serve as the CO_2-philic portion of CO_2-soluble surfactants, dispersants, thickeners, and chelating agents. CO_2−PPGMBE isothermal pressure−composition phase diagrams were determined at 298 K for PPGMBE average molecular weights of 340, 1000, and 1200. All the diagrams share the same features of one vapor−liquid−liquid three-phase equilibrium line and three two-phase equilibrium regions. The mixture critical points for the pseudobinary solutions were determined to be (7.2, 31.0, and 41.7) MPa for molecular weights of 340, 1000, and 1200, respectively.

Introduction

Dense carbon dioxide has been promoted as a sustainable solvent for a variety of applications, including polymerization,[1] polymer processing,[2] enzymatic reaction,[3] particle formation,[4] and generation of microcellular materials.[5] Although low molecular weight compounds exhibit certain solubility in liquid or supercritical CO_2 under tractable pressures,[6] CO_2 is a feeble solvent for polar and high molecular weight compounds. Therefore, neat CO_2 is often an unsatisfactory solvent, and CO_2-philic compounds must be introduced to the high-pressure CO_2 to enhance its effectiveness. For example, fluorous and siloxane-based polymers exhibited very high solubility in CO_2 and have been successfully employed as the CO_2-philic component of stabilizers for dispersion polymerizations,[1] for prospective CO_2-viscosity enhancement agents,[7] and for the generation of foams and fibers.[5,8] Fluorous and siloxane-based polymers are expensive, however. Further, fluorous polymers are particularly persistent (i.e., resistant to degradation) in the environment. Polymers composed solely of carbon, hydrogen, and oxygen are much more likely to be both inexpensive and biodegradable. Therefore, we propose the design of novel CO_2-soluble compounds that contain oxygenated hydrocarbon functional groups that exhibit high CO_2-philicity at moderate pressures. The CO_2-philicity of the methyl acetate group has been well established recently,[9–12] as illustrated by the remarkably high CO_2 solubility of poly(vinyl acetate),[13] sugar acetates,[12,14] oligo(vinyl acetate)-functionalized nonionic and ionic surfactants,[15,16] and oligo(vinyl acetate)-functionalized organometallic precursors for the generation of silver nanoparticles.[17] Unlike polyvinyl acetate, poly(propylene glycol) (PPG), which is also referred to as poly(propylene oxide), has been identified as a CO_2-philic compound that is readily available in reactive, oligomeric forms, making it an attractive candidate for the design of CO_2-soluble amphiphilic compounds. Ab initio molecular modeling calculations demonstrated that the bonding energy between CO_2 and ether oxygen is comparable with the energy when CO_2 interacts with the oxygen in a carbonyl group, which suggested ether oxygens are expected as important as carbonyl oxygens in facilitating CO_2 solubility.[18,19] Previous studies showed that PPG was much more soluble than poly(ethylene oxide) (PEO) in CO_2 for polymers with a comparable number of repeat units.[20,21] The pendent methyl group on each repeat unit in poly(propylene oxide) led to a lower cohesive energy density and surface tension that reduces the intermolecular interaction between polymer segments, resulting in a higher solubility of PPG versus PEO in CO_2. However, the solubilities of poly(butylene oxide), an ethyl-substituted PEO, and poly(tetrahydrofuran) with respect to PPG were smaller as evidenced by higher cloud point pressures at a given temperature. The solubility reduction for the poly(butylene oxides) could be attributed to the ethyl substitution adding a larger surface tension increment than the methyl substitution.[20] In the case of poly(tetrahydrofuran), the addition of methylene units in the backbone diluted the effect of the CO_2-philic ether oxygen versus PPO.[21] The phase behaviors of a variety of polyether block copolymers were also studied. Without surprise, the solubility values of the block polymers decreased with an increase in the PEO/PPG ratio for a given molecular weight.[20] Sarbu et al. synthesized a poly(ether-carbonate) copolymer from PPG and CO_2, in which ethers provided high flexibility and high free volume to enhance the entropy mixing, and the carbonyl groups in carbonate segments which formed a Lewis acid−Lewis base interaction with CO_2 favored the enthalpy mixing. The phase behavior study showed that the poly(ether-carbonate) copolymer with 15.4% carbonate groups and 250 repeat units was even more CO_2-soluble than a fluoroether polymer with an equivalent number of repeat units.[22] Single-tailed poly(propylene glycol) monobutyl ether (PPGMBE)-based ionic surfactants have been successfully developed

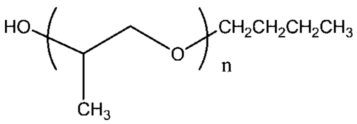

Figure 1. Structure of poly(propylene glycol) monobutyl ethers.

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Table 1. Phase Equilibrium Data for CO_2 + PPGMBE Binary Systems with Different Polymer Molecular Weights

equilibrium state	PPGMBE conc. in CO_2 (c/wt %)	(p/MPa) Mn = 340	Mn = 1000	Mn = 1200
	0(V.P.)[a]	6.41	6.41	6.41
	1	6.52		
	2	6.43		
	3	6.41		
	4	6.48		
	5	6.52		
B.P.[b]				
	25	7.03		
	30	6.76	30.48	40.13
	40	6.25	26.89	33.92
	50	6.14	19.79	22.89
	60	5.72	9.17	11.31
	70	4.96	5.72	5.86
	80	3.83	3.86	4.31
D.P.[b]	1		11.58	16.55
	2		16.27	22.75
	3		19.65	27.44
	4		21.99	31.92
	5		23.99	34.20
	6		25.51	36.13
	7	6.76	26.75	37.65
	8		27.65	38.96
	9		28.41	39.99
	10	7.17	29.51	40.75
	15	7.31	31.23	42.27
	20	7.31	31.37	41.27
VL_1L_2		6.41	6.21	5.93
mixture critical point	23	7.24	31.03	41.71

[a] Vapor pressure of CO_2 at 298 K: 6.41 MPa (http://webbook.nist.gov/). [b] B.P., Bubble Point; D.P., Dew Point.

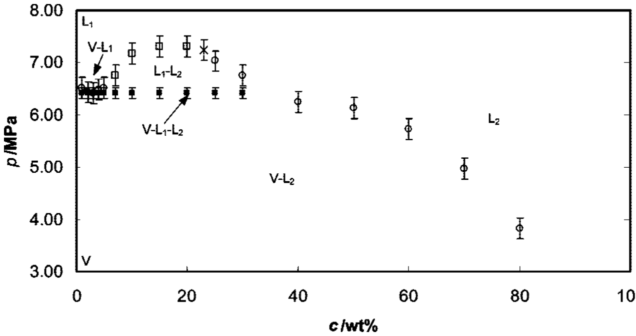

Figure 2. Pressure−composition isotherm at 298 K for the binary mixture of CO_2 with poly(propylene glycol) monobutyl ethers (PPGMBE, Mn = 340). □, ○, ■, and * represent dew point, bubble point, VL_1L_2 equilibrium point, and mixture critical point, respectively. (Same data markers are used in Figures 2, 3, and 4.)

by our group.[15] For example, at 313 K, PPGMBE 340 (MW of 340) sodium sulfate was approximately 0.5 wt % soluble in CO_2 at 54 MPa, and PPGMBE 1000 (Mn = 1000) pyridinium sulfate can dissolve in CO_2 at 0.5 wt % and 37 MPa.

Given the widespread use of PPO-based polymers,[23,24] the promising CO_2-solubility of several PPGMBE-based ionic surfactants,[15] and the relative ease that PPGMBE has participating in reactions that can form block copolymers and amphiphilic compounds, the objective of this research was to determine the phase behavior of PPGMBE in CO_2 in a large range of polymer concentrations.

Experimental Section

Materials. Poly(propylene glycol) monobutyl ethers (PPGMBE, Mn = 340, 1000, and 1200) were purchased from Aldrich and used as received, whose structure is shown in Figure 1. Carbon dioxide (99.99 %, Coleman grade) was obtained from Penn Oxygen.

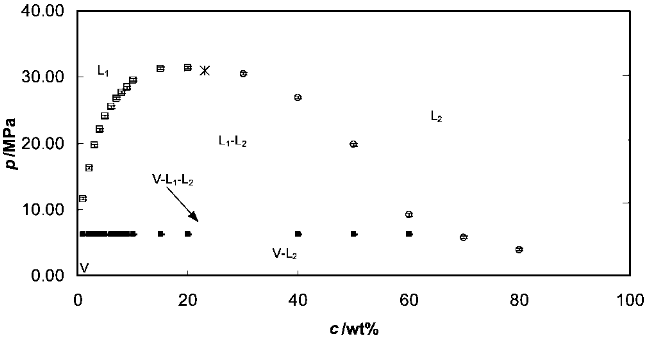

Figure 3. Pressure−composition isotherm at 298 K for the binary mixture of CO_2 with poly(propylene glycol) monobutyl ethers (Mn = 1000).

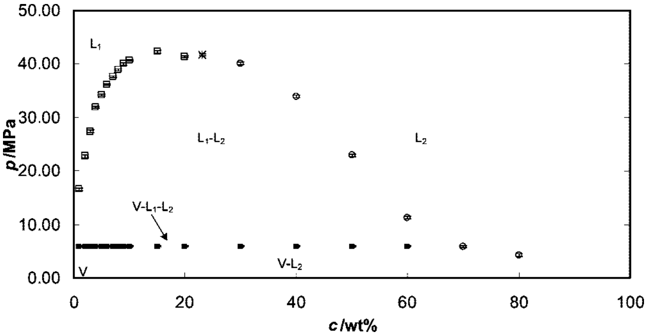

Figure 4. Pressure−composition isotherm at 298 K for the binary mixture of CO_2 with poly(propylene glycol) monobutyl ethers (Mn = 1200).

Phase Behavior Measurements. The equipment and techniques used to obtain cloud point pressures of CO_2−polymer mixtures have been described previously.[12,25] A nonsampling technique involving slow isothermal expansions of mixtures of specified overall composition was used to measure the cloud point pressure via visual determination of the pressure associated with the onset of the transformation of a transparent single phase to an opaque two-phase mixture. Bubble point pressures were associated with the first appearance of the less-dense phase at the top of the sample volume.

The mass of PPGMBE added to the sample volume was determined to within 0.0001 g (e.g., 2.0000 g ± 0.0001 g). The mass of the liquid CO_2 was determined as the product of the volume of CO_2 displaced from a positive displacement pump (± 0.01 cm^3) by the density of the liquid CO_2 at the injection temperature (± 0.1 K) and pressure (± 0.01 MPa). Up to 523 K and 30 MPa, the density of CO_2 was determined to within ± 0.03 % to ± 0.05 % using a new equation of stat with the consideration of the residual part of Helmholtz free energy.[26] As a result of these uncertainties, the polymer bubble point and dew point concentrations were precise to within about ± 1 % of the specified value (e.g., (5.0 ± 0.05) wt %). The pressures for two-phase boundaries were measured three times, with a reproducibility of ± 0.2 MPa. Three-phase pressures were also recorded three times, with a reproducibility of ± 0.1 MPa. Experiments were conducted over a range of concentrations by adding only CO_2 to the mixture, thereby decreasing the PPGMBE concentration in the mixture. The polymer concentration of the critical point was approximated as being intermediate to the polymer concentration associated with the last bubble-point measurement and the first dew point measurement shown

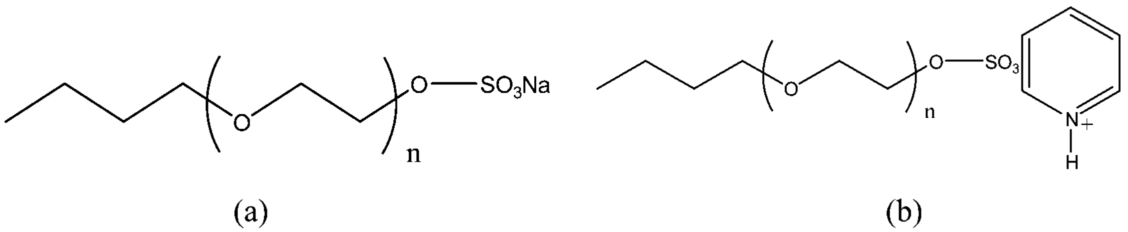

Figure 5. CO_2-soluble ionic surfactants using PPGMBE synthesized previously in our group. (a) PPGME (Mn = 340) sodium sulfate (n = ~5), (b) PPGME (Mn = 1000) pyridinium sulfate (n = ~16).[15]

in Table 1. Therefore, the uncertainty of the critical point polymer concentration was roughly ± (2 to 5) wt %.

Results and Discussions

The isothermal pressure−composition phase behaviors of PPGMBE 340, 1000, and 1200 at 298 K are shown in Figure 2, Figure 3, and Figure 4, respectively, over a much wider range of PPGMBE concentrations, from (0 to 80) wt %. Table 1 lists the dew points, bubble points, VL_1L_2 equilibrium points, and the mixture critical points obtained in this study. VL_1L_2 equilibrium (V, L_1, and L_2 represent the CO_2-rich vapor phase, CO_2-rich polymer solution, and polymer-rich solution, respectively) was observed at 6.41 MPa when expanding the CO_2 solution of PPGMBE with an Mn of 340 $g \cdot mol^{-1}$. Three two-phase equilibrium regions, VL_1, VL_2, and L_1L_2, are bounded by this VL_1L_2 line. The critical point for the binary mixture was estimated to be about 7.2 MPa between 20 wt % and 25 wt %, where the bubble point locus transitioned to a dew point locus with increasing polymer concentration in the mixture.

For PPGMBE 1000 and 1200, expansion of single-phase solutions resulted in L_1L_2 and, upon further expansion, VL_1L_2 equilibrium. However, the VL_1 region was not observed because of its small size. The L_1L_2 equilibrium pressures dramatically increase with increasing concentration and molecular weight. The mixture critical points were observed around (31.0 and 41.7) MPa near 23 wt % for PPGMBE with 1000 and 1200, respectively. The critical points were plotted on the L_1L_2 lines as shown in Figures 3 and 4.

The VL_1L_2 equilibrium pressures were found decreasing from 6.41 MPa, 6.21 MPa, then to 5.93 MPa with an increase of molecular weight from 340, 100, to 1200, respectively. The two-phase equilibrium pressures dramatically increase with increasing concentration and molecular weight, as confirmed by numerous publications.[21,27,28] As PPGMBE concentrations increase from (60 to 100) wt %, all the curves converge as they approach the very low vapor pressure of the PPGMBE compounds and terminate at the vapor pressure of PPGMBE at 100 wt % PPGMBE.

We previously generated ionic surfactants from PPGMBE, as shown in Figure 5. The associated phase behavior results, illustrated in Figure 6, confirm that the cloud point pressure is strongly related to the end group. Replacing the mildly CO_2-phobic hydroxyl end group with highly CO_2-phobic ionic groups, PPGMBE-based sodium sulfate and pyridium sulfate dramatically increased the miscibility pressure due to the sharp increase in the intra- and intermolecular interactions by ionic interaction.[15] Although PPGMBE is miscible with CO_2 in all proportions, these two ionic surfactants with PPGMBE tails had a limiting solubility of about 0.5 wt % in CO_2. In light of the fact that nearly all conventional hydrocarbon-based ionic surfactants are sparingly soluble or insoluble in CO_2, the surfactants shown in Figure 5 are considered to be CO_2-soluble.

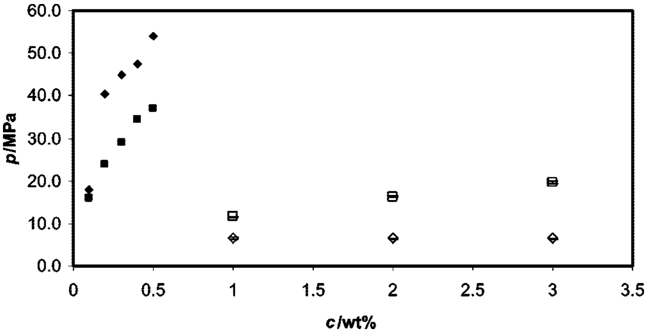

Figure 6. Comparison of the solubility of PPGMBE (measured at 298 K) with the PPGMBE-based surfactants (measured at 313 K) in CO_2.[15] ◇, ◆, □, and ■ represent the miscibility pressure of PPGMBE (Mn = 340), PPGMBE 340 sodium sulfate, PPGMBE (Mn = 1000), and PPGMBE 1000 pyridium sulfate, respectively.

Conclusions

Pressure−composition diagrams for mixtures of CO_2 with PPGMBE have been reported at 298 K. In all cases, the phase behavior diagram is characterized by a small VL_1 region, a L_1L_2 region with a mixture critical point, a three-phase VL_1L_2 equilibrium line, and a VL_2 low-pressure region. The results demonstrate that PPGMBE is extremely CO_2-soluble. Complete miscibility with CO_2 in all proportions can be achieved at the L_1L_2 critical pressure of (7.2, 31.0, and 41.7) MPa for PPGMBE molecular weights of 340, 1000, and 1200, respectively. Because PPGMBE is terminated with a reactive primary alcohol group, it is the possible design of CO_2-soluble compounds that includes PPGMBE as the CO_2-philic tail. For example, PPGMBEs with molecular weights of 340 and 1000 were used as the CO_2-philic segment in the synthesis of ionic surfactants that were about 0.5 wt % soluble in dense CO_2 at 298 K.

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