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Solubility of Poly(β-hydroxybutyrate) in Supercritical Carbon Dioxide

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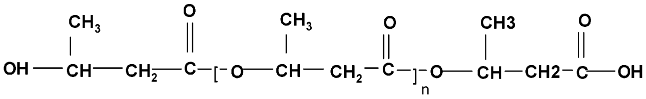
The equilibrium solubility of poly(β-hydroxybutyrate) (PHB) in supercritical carbon dioxide was studied. The effects of the main parameters such as pressure, temperature, and solvent density on solubility were determined at temperatures ranging from (308 to 348) K and pressures from (122 to 355) bar. The measured solubility was correlated using the model proposed by Chrastil.

Introduction

In recent years there has been a tremendous amount of attention paid to the area of supercritical fluid (SCF) extraction. This interest has been followed by changes in environmental regulations; therefore, conventionally used solvents are being replaced by “cleaner” processes such as those which utilize a SCF. Properties of SCFs that are interesting from an extraction viewpoint include the diffusion coefficient, the density, and the viscosity. Faster diffusion leads to more efficient separations than liquid facilitates. The low viscosity and the absence of surface tension in SCFs increase the speed of percolation. Thus, the passage of the solvent into the interstices of the matrix is enhanced. The solvent strength of the SCF is related to the density; thus, we have the opportunity to tailor the solvating characteristics of the SCF by controlling the pressure and/or temperature of the fluid. From a process standpoint, the sharp decrease in polymer solubility by decreasing pressure makes SCF solvents amenable for process recycles. The rapid disengagement of the gaseous supercritical solvent at low pressure promotes facile recovery of a solvent free polymer. Among the supercritical fluids, carbon dioxide is usually preferred; its advantages as a solvent are its low critical temperature and pressure, nonflammability, nontoxicity, and the facility of recovery of the solubilized product after precipitation by decreasing the pressure or heating.[1]

Many reports have emerged describing the potential of using supercritical solvents to fractionate and purify polymers with respect to molecular weight, chemical composition, and the backbone structure.[1−10] Information of solubility in SCFs is perhaps the most important thermophysical property that must be determined and modeled in order to design the extraction processes based on supercritical solvents. The available solubility data of some polymers in supercritical CO_2 are presented in Table 1.

This work was undertaken to determine the solubility of a very high molecular mass polymer ($\bar{M} = 800\,000$) such as poly(β-hydroxybutyrate) (PHB) in supercritical carbon dioxide for the first time. The structure of the polymer is shown in Figure 1. PHB, which is a biodegradable and biocompatible thermoplastic, has broadly similar physical properties to those of polypropylene.[11] It is one of the most important microbial polyesters belonging to the poly(hydroxyalcanoate) group. It has many applications in medicine, veterinary practice, and agriculture due to its biodegradability.[12] Currently the main problem, which limits the widespread use of PHB and its copolymers, is its relatively high cost compared to that of polypropylene. The fermentation process, substrates, and product recovery are the major costs.[13] In this research the solubility of PHB in supercritical CO_2 (for further study in the development of a low cost and effective downstream process for PHB extraction) was investigated. The solubility data were correlated using a semiempirical model proposed by Chrastil.[14]



$HO-\overset{\overset{CH_3}{|}}{CH}-CH_2-\overset{\overset{O}{\|}}{C}-[-O-\overset{\overset{CH_3}{|}}{CH}-CH_2-\overset{\overset{O}{\|}}{C}-]_n-O-\overset{\overset{CH3}{|}}{CH}-CH2-\overset{\overset{O}{\|}}{C}-OH$

Figure 1. Structure of poly(β-hydroxybutyrate).

Experimental Section

Materials. Ethanol stabilized chloroform, methanol, and sulfuric acid (Aldrich) were used as received. Carbon dioxide (Sabalan, Tehran, 99.99%) was used in all extraction experiments. Poly(β-hydroxybutyrate) (Aldrich) was used as received.

Procedure. A Suprex (Pittsburgh, PA) MPS/225 system equipped with a modified static system for solubility determination in supercritical fluid extraction mode was used. A schematic diagram of the modified static system used in this study is shown in Figure 2. Detailed descriptions of the equipment and operating procedure are given in refs 15−17. Solubility measurement was accomplished with a 1 mL extraction vessel in the pressure range from (122 to 355) bar at the temperatures (308, 318, 328, 338, and 348) K for a duration of 30 min. The solid polymer (100 mg) was mixed well with some 0.9 g of glass beads and packed into the extraction vessel. This procedure prevents channeling, increases the contact surface between the sample and the SCF, and consequently, reduces the equilibration time. Sintered stainless steel filters (5 μm) were used to prevent any carryover of the solute. Supercritical CO_2 was pressurized and passed into vessel D

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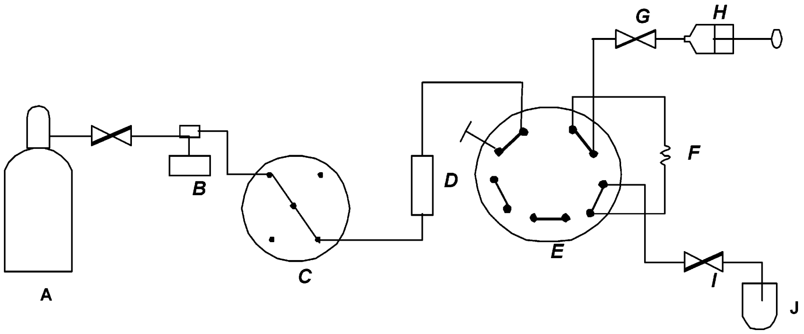

Figure 2. Schematic diagram of experimental apparatus for measuring solubility: (A) CO_2 gas tank; (B) supercritical fluid pump; (C) 5-port, 4-position valve; (D) 1 mL equilibrium cell; (E) 10-port, 2-position valve; (F) injection loop; (G) on/off valve; (H) syringe; (I) microadjust valve; (J) collection vial.

Table 1. Solubility of Polymers in Supercritical CO_2

polymer	T/K	P/bar	molecular mass/$\bar{M}$	conc (%)	source
poly(propylene)	436−481	456−861		6−38	1
poly(butene-1)	404−423	304−912		6−38	1
Nylon-6	506−514	405−517		13−16	1
glycidyl azide polymer	318	345−655		0.04−0.11	1
poly(ethylene glycol)	313	100		0.25	6
(PEG)	313	284		0.88	6
PEG nonphenyl ether	318−338	120−300	2 500	0.01−0.65	9
PEG (in CO_2−ethanol)	313	160	1 000	0.15−0.45	27
poly(methyl acrylate)	293−473	1700−2200	30 700	5	23
poly(ethyl acrylate)	323−473	1200−1300	119 300	5	23
poly(propyl acrylate)	373−453	1200−1500	140 000	5	23
poly(butyl acrylate)	353−473	1000−3000	61 800	5	23
poly(etylhexyl acrylate)	353−493	1100−3000	112 800	5	23
poly(octadecyl acrylate)	483−533	1000−2600	23 300	5	23
poly(butyl methacrylate)	393−503	1100−3000	320 000	5	23
poly(L-lactide)	328−338	up to 200	2 000	0.10−0.40	26, 28
poly(L-lactide)	328	250	5 500	0.22	28

through the 5-port, 4-position valve C. After equilibrium was obtained at the desired temperature and pressure, which took about 30 min, a 122 μL portion of the saturated supercritical CO_2 was loaded into injection loop F by means of a 10-port, 2-position valve, E. Then the loop was depressurized into the collection vial, J, containing a known volume of chloroform, by switching the injection valve, E. To prevent solvent dispersal, the depressurizing rate of the sample loop was adjusted by valve I. Finally, valves C and I were opened completely, and the sample loop was washed with some chloroform and collected into collection vial J. It should be noted that, by monitoring the solubility data versus time, 30 min was found to be adequate to ensure the attainment of equilibrium. The equilibrium temperature and pressure were measured with an accuracy of ±1 K and ±0.5 bar, respectively. To determine the PHB concentration, 2 mL of solution was subjected to methanolysis in the presence of 3% (v/v) sulfuric acid according to the Brandl method.[18] Gas chromatography of the resulting methyl ester of the constituent 3-hydroxybutyrate was performed with a Philips scientific model 44100 gas chromatograph equipped with a flame ionization detector (FID) and an on-column injector. A stock solution of PHB (1000 $\mu g \cdot cm^{-3}$) was prepared by dissolving the appropriate amount of the solid sample in chloroform. A set of standard solutions was then prepared by appropriate dilution of the stock solution. The obtained calibration curve was used to determine the concentration of the PHB in the collection vial.

The nitrogen flow rate through the PEG-20M packed column was 30 $mL \cdot min^{-1}$. The flame ionization detector was supplied with 330 $mL \cdot min^{-1}$ of air and 30 $mL \cdot min^{-1}$ of hydrogen. The injection and detector temperatures were (453 and 573) K, respectively. The initial column temperature was 363 K (maintained for 1 min), with increases of 8 $K \cdot min^{-1}$ to a final temperature of 423 K (maintained for 5 min). Benzoic acid was used as internal standard. The retention times of the methyl esters of 3-hydroxybutyrate (HB) and benzoic acid were (3.7 and 7.2) min, respectively.

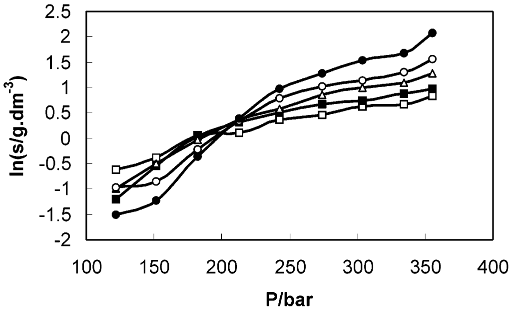

Figure 3. Solubilities of PHB in supercritical CO_2 vs pressure: (□) 308 K; (■) 318 K; (△) 328 K; (○) 338 K; (●) 348 K.

Results and Discussion

The reliability of the apparatus was preliminarily checked by measuring the solubility (mole fraction, y) of naphthalene in supercritical CO_2 at 308 K, as was described before.[15−17] The solubilities of the polymer at the temperatures (308, 318, 328, 338, and 348) K and in the pressure range from 122 to 355 bar were determined. The resulting solubilities, s, in terms of grams per liter of the solute in supercritical carbon dioxide are summarized in Table 2. These results are also shown graphically in Figure 3. The solubility data were generally reproducible within ±5%, given as a standard deviation of replicate measurements.

Table 2 reveals that the solubility of the solute increases with increasing pressure at constant temperature, with the

Table 2. Solubility of PHB in Supercritical CO_2[a]

P/bar	ρ/g·dm^{-3}	s/g·dm^{-3}	P/bar	ρ/g·dm^{-3}	s/g·dm^{-3}
		T/K = 308			
122	771	0.54	274	916	1.58
152	818	0.68	304	931	1.86
182	850	1.07	334	946	1.96
213	876	1.13	355	955	2.41
243	897	1.46			
		T/K = 318			
122	661	0.31	274	875	1.98
152	745	0.58	304	893	2.11
182	792	1.06	334	910	2.43
213	826	1.37	355	919	2.65
243	852	1.67			
		T/K = 328			
122	504	0.23	274	831	2.38
152	657	0.59	304	853	2.69
182	726	1.05	334	872	2.98
213	771	1.44	355	884	3.49
243	804	1.79			
		T/K = 338			
122	398	0.18	274	786	2.78
152	561	0.43	304	812	3.18
182	654	1.01	334	834	3.69
213	712	1.43	355	848	4.77
243	754	2.23			
		T/K = 348			
122	327	0.15	274	740	3.65
152	477	0.29	304	772	4.71
182	585	0.69	334	796	5.33
213	652	1.49	355	811	8.01
243	702	2.65			

[a] The computer system of Suprex MPS/225 will show the density calculations of CO_2 directly according to the Pitzer method.[24,25]

influence of pressure on the solubility being more pronounced at higher temperatures. This is in accord with the conventional wisdom stating that the density of a supercritical fluid must increase in order to increase the solubility and extraction efficiency.[19] The effect of temperature on the solubility of PHB as shown in Figure 3 indicates that the retrograde solubility (crossover/pressure effect) behavior for the polymer exists in the supercritical state. The same behavior was reported for different organic compounds previously.[20−22] At pressures above the crossover region (182 bar), solubility increases with increasing both pressure and temperature, while, below this point, solubility increases with increasing pressure but decreases with increasing temperature. At lower pressure, the fluid density is lowered by a small increase in temperature. Since the density effect is predominant in this region, the solubility will decrease with increasing temperature. However, at higher pressure the fluid density is less dependent on temperature so that the observed increase in solubility with temperature could be primarily due to other factors, especially the higher vapor pressure of the solid samples.

The experimental solubility data for PHB are correlated using the model proposed by Chrastil.[14] This model is based on the hypothesis that each molecule of a solute (S) associates with k molecules of supercritical solvent (C) to form a solvated complex (SC_k), which is in equilibrium with the gas. The model proposes a linear relationship between the logarithm of the solubility, s/g·dm^{-3}, and the logarithm of the fluid density, ρ/g·dm^{-3}, given by

$$\ln(s) = k\,\ln(\rho) + a/T + b \qquad (1)$$

where $a = \Delta H/R$ and $b = -\ln[M_C{}^k/(M_S + kM_C)] + q$, where s is the solubility, ρ is the fluid density, T is the temperature, k is the dissociation number, ΔH is the total enthalpy of reaction (i.e., enthalpy of solvation plus enthalpy of vaporization of the solute), q is a constant, and M_S and M_C are the molecular weights of the solute and solvent, respectively. ln(s) is a linear function of $1/T$ at constant density. The value of b can be chosen to minimize the deviation of the model from experimental data. The optimum values of k, a, and b for poly(β-hydroxybutyrate) are given in Table 3.

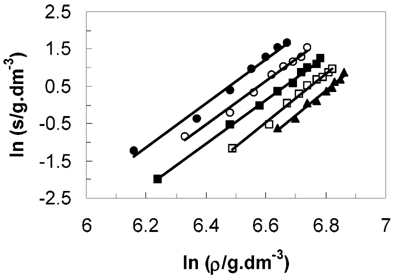

Figure 4. PHB solubility vs density of supercritical CO_2: (▲) 308 K; (□) 318 K; (■) 328 K; (○) 338 K; (●) 348 K.

Table 3. Solubility Constants of the Chrastil Model for Poly(β-hydroxybutyrate) in Supercritical CO_2

compound	k	a	b
poly(β-hydroxybutyrate)	6.192	−26137	52.11

The solubility data obtained in this study show the expected linear relationship correlated by the Chrastil model. Sample plots of ln(s) versus ln(ρ) for poly(β-hydroxybutyrate) at various temperatures are shown in Figure 4. The straight lines in Figure 4 are the best fit of eq 1 to the solubility data. The average absolute relative deviation (AARD) between experimental data and the model calculation was obtained with the equation

$$\%\text{AARD} = 1/n\sum|(y_{i,\text{exp}} - y_{i,\text{cal}})/y_{i,\text{exp}}| \qquad (2)$$

where $y_{i,\text{exp}}$ is the experimental solubility, $y_{i,\text{cal}}$ is the solubility obtained from a least squares plot, and n is the number of total experiments. The values of AARD are in the range (8.15 to 29.44)%. The slopes of the solubility isotherms are equal within a good approximation.

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