Measurement and Modeling of the CO_2 Solubility in Poly(ethylene glycol) of Different Molecular Weights

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The solubility of supercritical carbon dioxide ($scCO_2$) in solid (298 K) and melted (323 K) poly(ethylene glycol) (PEG), in the pressure range (7 to 25) MPa, was measured using a magnetic suspension balance. The phase behavior of the CO_2 + PEG system was modeled by using the Sanchez−Lacombe equation of state (EOS) and statistical associating fluid theory (SAFT). The results show a good solubility of CO_2 in polymer and a good accuracy of the thermodynamic models in describing the phase equilibrium of the working system. The experimental data are also in good agreement with the solubility values previously described in the literature, obtained by employing different experimental techniques.

Introduction

Poly(ethylene glycol) (PEG) is a condensation polymer of ethylene oxide, having the general formula $H(OCH_2CH_2)_nOH$, where n is the average number of repeating oxyethylene units ($n = 4$ to 180). The low relative molecular mass compounds (MW < 700) are colorless, odorless, viscous liquids, while compounds with relative molecular mass higher than 1000 are waxlike solids or solids.

PEGs are water-soluble polymers and are widely used in the pharmaceutical and cosmetic industries because of their physiological acceptance.[1] Its hydrophilicity, antithrombogenicity, and good biocompatibility recommend PEG for biomedical applications, such as drug delivery devices[2–8] and tissue engineering scaffolds.[5]

The traditional methods for polymer processing involve either high temperatures, necessary for melting or viscosity reduction, or hazardous volatile organic solvents (VOCs) and chlorofluorocarbons (CFCs). Due to the undesirable environmental impact of these solvents, extensive research is focused on seeking new and cleaner methods for the processing of polymers.

One such method is the use of supercritical fluids as processing solvents or plasticizers. The special combination of gaslike viscosity and diffusivity and liquid-like density and solvating properties of a supercritical fluid makes it an excellent solvent for various applications.[5]

Supercritical carbon dioxide ($scCO_2$) is the preferred choice for these applications, due to its properties. It is nontoxic, nonflammable, chemically inert, environmentally safe, and inexpensive. Its supercritical conditions ($T_c = 304.1$ K, $P_c = 7.38$ MPa) are easily attained; it can be removed from a system by simple depressurization; and it dissolves better in some polymers than other supercritical fluids (e.g., propane or nitrogen).[1,5,9]

$scCO_2$ is a good solvent for many low molecular weight compounds and a few polymers. Its solubility in many polymers is substantial, being influenced by temperature, pressure, and, sometimes, weak interactions with the groups in the polymer. Dissolved CO_2 causes a reduction in the viscosity of the polymers, by increasing their free volume. Thus, the polymers are plasticized, allowing processing at lower temperatures.

$scCO_2$ was used as solvent or antisolvent for obtaining PEG microparticles used as drug carriers.[6,8–11] The technique offers two important advantages. The first advantage refers to a better control of particle size, particle size distribution, and morphology, which can be achieved by tuning process parameters such as the amount of dissolved CO_2, temperature, pressure, nozzle diameter, and depressurization rate.[12] The second advantage refers to the lack of organic solvent or, when necessary, the efficient removal and recovery of the solvent. This allows sensitive bioactive molecules, such as proteins and drugs, to be introduced during polymer processing stages.[12]

Despite the huge potential of $scCO_2$ as a processing solvent for PEG, experimental data on the solubility of CO_2 in PEG, essential for process design, are quite scarce.[1,13] On this basis, the present work tries to contribute to the understanding of CO_2 + PEG phase equilibrium by studying the solubility data obtained by a magnetic suspension balance. Thermodynamic models (Sanchez−Lacombe equation of state and the statistical associating fluid theory (SAFT)) were used to correlate and predict phase equilibrium, and their reliability was subsequently evaluated.

Experimental

Materials. Poly(ethylene glycol) (PEG) of different molecular weights (PEG 1500 and PEG 4000) was obtained from Merck, Germany, and was used without further purification.

Carbon dioxide (CO_2) was obtained from Messer, Slovenia, and was used without further purification.

Experimental Equipment. For determining the solubility of CO_2 in PEG, a magnetic suspension balance (MSB-RUBOTHERM) was used. A detailed description of the device and of the working procedure can be found in the literature.[14]

The MSB allows the gravimetric measurement (with an uncertainty $u_c = 10$ μg) of the quantity of gas dissolved in the polymer, over a wide range of temperatures and pressures. This is possible due to the location of the balance outside the measuring cell, in normal conditions of pressure and temperature.

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Table 1. Sanchez−Lacombe EOS Characteristic Parameters (P^*, Characteristic Pressure; ρ^*, Characteristic Density; T^*, Characteristic Temperature) for CO_2 and PEG[20,21]

	P^* MPa	ρ^* $kg \cdot m^{-3}$	T^* K	ref
CO_2	369.1	1253.0	341.2	20,21
PEG	635.7	1183.2	635.5	21

The solubility was measured for both solid ($T = (298 \pm 0.2)$ K) and melted ($T = (323 \pm 0.2)$ K) polymers in the pressure range (7 to 25) MPa (with an uncertainty $u_c = 0.005$ MPa). The pressure range was chosen to match previous solubility measurement conditions. A comparison was made among obtained experimental values, data existing in the literature, and the results of thermodynamic modeling.

Thermodynamic Models. The ASPEN Polymer Plus program was used for modeling the phase behavior of the CO_2 + PEG system. The commonly used equations of state (EOS) for polymer/CO_2 systems are based either on the perturbed hard chain theory or on the lattice model.

Sanchez−Lacombe (S−L) EOS. One such model based on the lattice theory is the one proposed by Sanchez and Lacombe.[15,16] According to this model, a fluid is viewed as a combination of molecules and holes confined to the sites of a lattice. A detailed description of the S−L model can be found in the literature.[17,18]

The S−L EOS is written as[19]

$$\tilde{\rho}^2 + \tilde{P} + \tilde{T}\left[\ln(1-\tilde{\rho}) + \left(1 - \frac{1}{r}\right)\tilde{\rho}\right] = 0 \qquad (1)$$

$$\tilde{P} = \frac{P}{P^*} \quad \tilde{\rho} = \frac{\rho}{\rho^*} \quad \tilde{T} = \frac{T}{T^*} \quad r = \frac{MP^*}{RT^*\rho^*} \qquad (2)$$

where P^*, ρ^*, and T^* are the characteristic parameters for the pure substance; r is the size parameter, representing the number of lattice sites occupied by a molecule; and M is the molecular weight.

The characteristic parameters for CO_2 and PEG are given in Table 1.

The characteristic parameters of the pure compounds are obtained by fitting eq 1 to the PVT data of each component. For mixtures, these parameters are determined using a mixing rule.[14]

$$P^* = \sum_i \sum_j \varphi_i \varphi_j P_{ij}^* \qquad (3)$$

$$P_{ij}^* = (1 - k_{ij})(P_i^* P_j^*)^{0.5} \qquad (4)$$

$$T^* = P^* \sum_i \frac{\varphi_i^0 T_i^*}{P_i^*} \qquad (5)$$

$$\frac{1}{r} = \sum_i \frac{\varphi_i^0}{r_i} \qquad (6)$$

$$\varphi_i^0 = \frac{\varphi_i P_i^*/T_i^*}{\sum_j (\varphi_j P_j^*/T_j^*)} \qquad (7)$$

$$\varphi_i = \frac{w_i/\rho_i^*}{\sum_j (w_j/\rho_j^*)} \qquad (8)$$

where w_i is the mass fraction of the component i in the mixture.

In eq 4, k_{ij} is a binary interaction parameter which is determined by fitting eqs 1 to 8 to experimental data to minimize the relative deviation between experimental and calculated solubility.

Table 2. SAFT Characteristic Parameters (m, Number of Segments; u_0/k, Segment Dispersion Energy; v_{00}, Volume of the Segment) for CO_2 and PEG[1]

	u_0/k K	v_{00} $cm^3 \cdot mol^{-1}$	m
CO_2	216.08	13.578	1.417
PEG	342.68	13.159	MW/24.7033

Statistical Associating Fluid Theory (SAFT). The SAFT EOS is a thermodynamic model for polymer systems, based on the perturbation theory of fluids. This equation of state accounts for chain formation, dispersion interactions, molecular repulsion, and association due to hydrogen bonding or other specific forces.[22]

The effect of the molecular structure and interactions on the bulk properties and phase behavior of pure compounds and mixtures is expressed as the sum of contributions to the Helmholtz free energy (A).[23]

$$A = A_{\text{ideal}} + A_{\text{hardsphere}} + A_{\text{chain}} + A_{\text{disp}} + A_{\text{assoc}} \qquad (9)$$

A_{ideal} is the ideal free energy of the mixture; $A_{\text{hardsphere}}$ is the hard-sphere contribution; A_{chain} is the increment due to bonding; A_{disp} is the contribution of dispersion interactions between segments; and A_{assoc} is the cross-association effect.

The residual term (A_{res}) of expression 9

$$A_{\text{res}} = A - A_{\text{ideal}} \qquad (10)$$

represents the basis for developing the SAFT EOS. Further details about this model are given in the original publications[24−28] and will not be repeated here.

For phase equilibrium prediction, the SAFT EOS requires three parameters, which are the number of segments (m), the segment dispersion energy (u_0/k), and the volume of the segment (v_{00}).[1] Huang and Radosz[26] fitted the model to vapor pressure and liquid density data, and they obtained values of the pure component parameters for a large number of components.

The pure component parameters for CO_2 and PEG were taken from the literature[1] and are given in Table 2.

For mixtures, the SAFT EOS has a form identical to that for pure substances. However, mixing rules are necessary to calculate the corresponding characteristic parameters.[27] Similar to the S−L EOS, a binary interaction parameter, k_{ij}, is used to minimize the relative deviation between experimental solubility data and the values estimated by using the SAFT EOS.

Results and Discussion

The solubility data are presented in Figures 1 and 2 (the experimental values are shown in Supporting Information). The values for CO_2 solubility in PEG are in good correlation with other experimental data.[1,10,13] In the present work, the experimental data were obtained by gravimetric measurements, performed with MSB, and the literature data were obtained by a static analytic method.[13]

As stated also in other sources,[1,9,13,28] the solubility of CO_2 in polymer increases with increasing pressure. This phenomenon can be explained by the plasticization effect of CO_2. By raising the pressure, the gas molecules are forced between polymer chains, expanding the space between molecules and thus increasing their mobility. Increased mobility of the chains allows more gas molecules to be adsorbed once the pressure is further raised.

The effect of chain mobility on CO_2 solubility is clearly illustrated by the difference between the values for solid and melted samples. Therefore, a higher mobility of the molecules

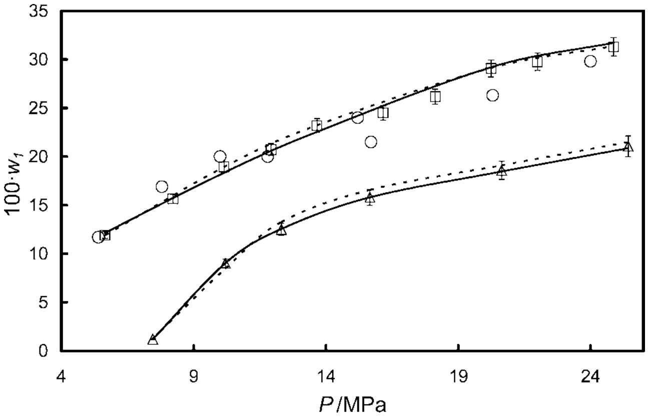

Figure 1. Solubility of CO_2 (1) in PEG 1500 (2). Comparison among data from the present work, from the literature, and from modeling results. □, solubility at 323 K (present work); ○, solubility at 323 K (literature);[13] Δ, solubility at 298 K (present work); —, S−L EOS modeling results; - - -, SAFT modeling results.

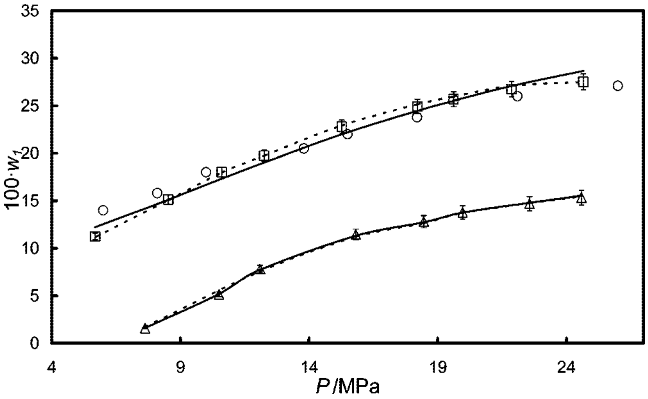

Figure 2. Solubility of CO_2 (1) in PEG 4000 (2). Comparison among data from the present work, from the literature, and from modeling results. □, solubility at 323 K (present work); ○, solubility at 323 K (literature);[13] Δ, solubility at 298 K (present work); —, S−L EOS modeling results; - - -, SAFT modeling results.

in the liquid form of the polymer accounts for the significantly higher solubility values.

Another explanation for the lower solubility of CO_2 in the solid polymer may refer to the presence of the crystalline phase. A linear polymer in the solid state may exhibit crystalline regions, where the packed configuration of the chains does not allow the penetration of gas molecules, the solubility in these regions being close to zero.

The effect of the molecular weight of the polymer on the gas solubility is presented in Figure 3.

One can notice that, at the same conditions of temperature, the difference in solubility is negligible for lower pressures (near the critical point of CO_2). This observation was also made by Wiesmet et al.[1,13] At higher pressures, however, this difference becomes significant. The difference is especially important for solid polymer samples. One explanation for this occurrence may be the difference in the density of the two polymers. A higher molecular weight, and thus a higher density, offers a reduced free volume to be occupied by the gas molecules.

At the same time, the number of interactions between the end-groups of the polymer chains and CO_2 molecules is higher for the lower molecular weight polymer. These interactions account for the good solubility of CO_2 in PEG and therefore for the possibility of using supercritical fluids for processing.

The behavior of the polymer−gas system was also predicted by using the S−L and SAFT models. Binary parameters of these equations of state were regressed using the Aspen Polymer simulation software and are given in Tables 3 and 4.

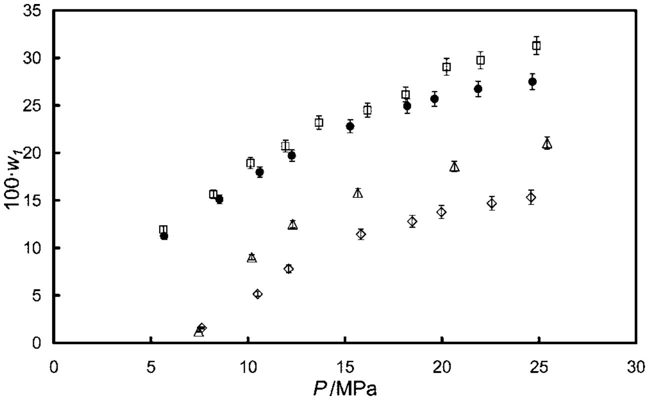

Figure 3. Effect of the molecular weight of the polymer on the CO_2 (1) solubility in PEG (2). □, solubility in PEG 1500 at 323 K; ●, solubility in PEG 4000 at 323 K; Δ, solubility in PEG 1500 at 298 K; ◇, solubility in PEG 4000 at 298 K.

Table 3. Sanchez−Lacombe EOS Binary Interactions Parameters, k_{ij}, Regressed with Aspen Plus for All Studied Systems (CO_2 + PEG 1500 and CO_2 + PEG 4000, at Both 323 K and 298 K)

sample	k_{ij}	standard deviation
PEG 1500, 323 K	0.0605	0.0125
PEG 1500, 298 K	0.1117	0.0212
PEG 4000, 323 K	0.0823	0.0074
PEG 4000, 298 K	0.1357	0.0157

Table 4. SAFT Binary Interactions Parameters, k_{ij}, Regressed with Aspen Plus for All Studied Systems (CO_2 + PEG 1500 and CO_2 + PEG 4000, at Both 323 K and 298 K)

sample	k_{ij}	standard deviation
PEG 1500, 323 K	0.0452	0.0010
PEG 1500, 298 K	0.1879	0.0157
PEG 4000, 323 K	0.0513	0.0007
PEG 4000, 298 K	0.1925	0.0075

Table 5. Percent Average Absolute Relative Deviation (AARD) of the Solubility Values Calculated with the Sanchez−Lacombe EOS and SAFT for the CO_2 + PEG Systems[a]

	AARD/%	
system	S−L EOS	SAFT
PEG 1500, 323 K	2.02	1.55
PEG 1500, 298 K	0.39	4.36
PEG 4000, 323 K	3.07	0.55
PEG 4000, 298 K	0.80	3.19

[a] $\mathrm{AARD} = 1/N\sum_{i=1}^{N} |w_{i(\mathrm{calcd})} - w_{i(\mathrm{exptl})}|/w_{i(\mathrm{exptl})}$.

For both models, the binary interaction parameter, k_{ij}, is dependent on the physical state of the polymer: the value of k_{ij} is significantly higher for the solid samples. The causes for this occurrence may be the same as accounting for the difference in solubility.

The value of k_{ij} slightly increases with the molecular weight for all the studied samples. These results are in agreement with the ones obtained by Wiesmet et al.[1]

Both models describe successfully the phase behavior for the CO_2 + PEG systems (Table 5). In the case of liquid samples, however, the SAFT model describes with better accuracy the solubility of CO_2 in the polymer, and the S−L EOS exhibits better results for the solid polymer. The higher reliability of the SAFT model for liquid polymers was previously mentioned in the literature.[17,29]

Conclusions

The solubility data obtained for the CO_2 + PEG system is in good agreement with other experimental results. The solubility is influenced by the physical state of the polymer, by pressure, and, at a smaller extent, by the molecular weight of the polymer. The modeling results prove the reliability of both the S−L EOS and SAFT for predicting the phase behavior of the system. However, when liquid polymers are involved, better results are obtained by applying the SAFT model. The value of the binary interaction parameters, used to correlate experimental and calculated data, depends on the physical state and molecular weight of the polymer sample. All of these results represent a step forward in understanding and predicting the thermodynamics of the stages involved in polymer processing by using supercritical carbon dioxide.

Supporting Information Available:

Experimental results for the solubility of CO_2 in poly(ethylene glycol) of molecular weight 1500 and 4000, measured for different values of temperature [(298 and 323) K] and pressure [(7 to 25) MPa]. This material is available free of charge via the Internet at http://pubs.acs.org.

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