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Solubility of Bisphenol A in Supercritical Carbon Dioxide

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ABSTRACT: The solubility of solid bisphenol A (4,4′-(propane-2,2-diyl)diphenol) in supercritical carbon dioxide (SC-CO_2) has been measured at temperatures of $T = 313$ K, $T = 333$ K, and $T = 353$ K and in the pressure range 12 MPa < P < 20 MPa, using a variable-volume view cell according to the synthetic method. The solubility increases with increasing pressure and temperature, ranging from $1.8 \cdot 10^{-5}$ (mole fraction) at $T = 313$ K and $P = 16.4$ MPa to $7.7 \cdot 10^{-5}$ (mole fraction) at $T = 353$ K and $P = 14.6$ MPa. The solubility data obtained have been correlated using the Peng–Robinson equation of state with quadratic mixing rules. The results obtained are useful for the design of processes for the synthesis or recycling of polycarbonate in supercritical CO_2.

INTRODUCTION

The unique properties of supercritical carbon dioxide (SC-CO_2) have been exploited in several polymer-processing techniques.[1] SC-CO_2 can interact with many polymeric materials, causing different variations in their physical properties, including reductions in melting and glass transition temperatures, polymer swelling, and increased polymer chain mobility or reductions of the viscosity of polymer melts.[2]

Polycarbonates (PC) are an important group of thermoplastic polymers used in many applications, including electronic components, data storage systems such as CDs and DVDs, plastic bottles, and construction materials. The two main routes of synthesis of PC are the interfacial polycondensation of bisphenol A (BPA, 4,4′-(propane-2,2-diyl)diphenol) with phosgene ($COCl_2$) and the melt transesterification of BPA with diphenyl carbonate (DPC).[3]

Different applications of supercritical fluids for PC processing have been proposed. Considering the increasing consumption of PC-based materials, suitable methods to recycle these materials are highly needed. Supercritical fluids can provide a favorable environment for the chemical recycling of PC by depolymerization into BPA and dimethyl carbonate.[4] SC-CO_2 can be used as a reaction medium for the depolymerization of PC and as an extraction medium for the fractionation of depolymerization products.[5] SC-CO_2 has also been used as a solvent for the solid-state polymerization of BPA[6] and for the synthesis of PC by transesterification between BPA and DPC,[7] applications in which the plasticization of PC with SC-CO_2 improves the mass transfer and the reaction rate. Furthermore, SC-CO_2 can be used to clean the PC obtained by the extraction of reaction byproduct as well as of unreacted BPA, whose presence in the polymer can cause negative effects for health in some applications.[8]

To develop these applications, it is necessary to obtain information about the phase behavior of the systems involved. The aim of this work is to contribute to this objective determining the solubility of solid BPA in carbon dioxide at supercritical conditions. In a previous work of Margon and co-workers,[9] the phase behavior of this system was determined in the temperature range 403.15 K ≤ T ≤ 473.15 K and the pressure range 2.4 MPa < P < 9.6 MPa, corresponding to the vapor–liquid equilibrium region between melted BPA and supercritical CO_2. This work complements the previous study presenting measurements in the temperature range 313 K ≤ T ≤ 353 K and pressure range 12 MPa < P < 20 MPa, thus corresponding to the solubility of solid BPA in SC-CO_2.

EXPERIMENTAL SECTION

Materials. Carbon dioxide (mass fraction composition of CO_2: 0.995) was provided by S. E. Carburos Metálicos S. A. (Spain). Bisphenol A with a minimum mass fraction composition of BPA of 0.99 was purchased from Sigma-Aldrich (Spain). All materials were used as received.

BPA samples were characterized by differential scanning calorimetry assays (DSC822e Mettler Toledo, sensor FRS5, heating rate 10 $K \cdot min^{-1}$ under N_2 60 $mL \cdot min^{-1}$ flow) to determine the temperature and enthalpy of melting. The measured melting temperature was 429.6 K with a melting enthalpy of 30.7 $kJ \cdot mol^{-1}$, in good agreement with the results of Price[10] (430 K and 31 $kJ \cdot mol^{-1}$, respectively).

Equipment. A schematic diagram of the equipment used for solubility determinations is shown in Figure 1. The main part of the equipment is an optical cell (SITEC 740.2120) with a variable volume between (11 and 25) mL. The volume is controlled by a piston displaceable by water pressurized with a manual pressure generator (SITEC 750.1060). The maximum operating conditions inside the cell are 50 MPa and 473 K. The cell has two opposite sapphire windows. Through one of them a cold light lamp is situated to allow the visualization of the different processes taking place inside the cell, aided by a CCD camcorder (Eurotechnica Ingenieurbüro GmbH) connected to a personal computer. The contents of the cell are mixed with a magnetic stirrer (AGIMATIC S). The internal temperature of the cell is controlled by a proportional–integral–derivative (PID) temperature controller (OMRON E5GN) acting over an electrical jacket and measuring the temperature with a J type thermocouple (SITEC 770.5131-22, uncertainty 0.1 K). The pressure is measured with a membrane pressure meter

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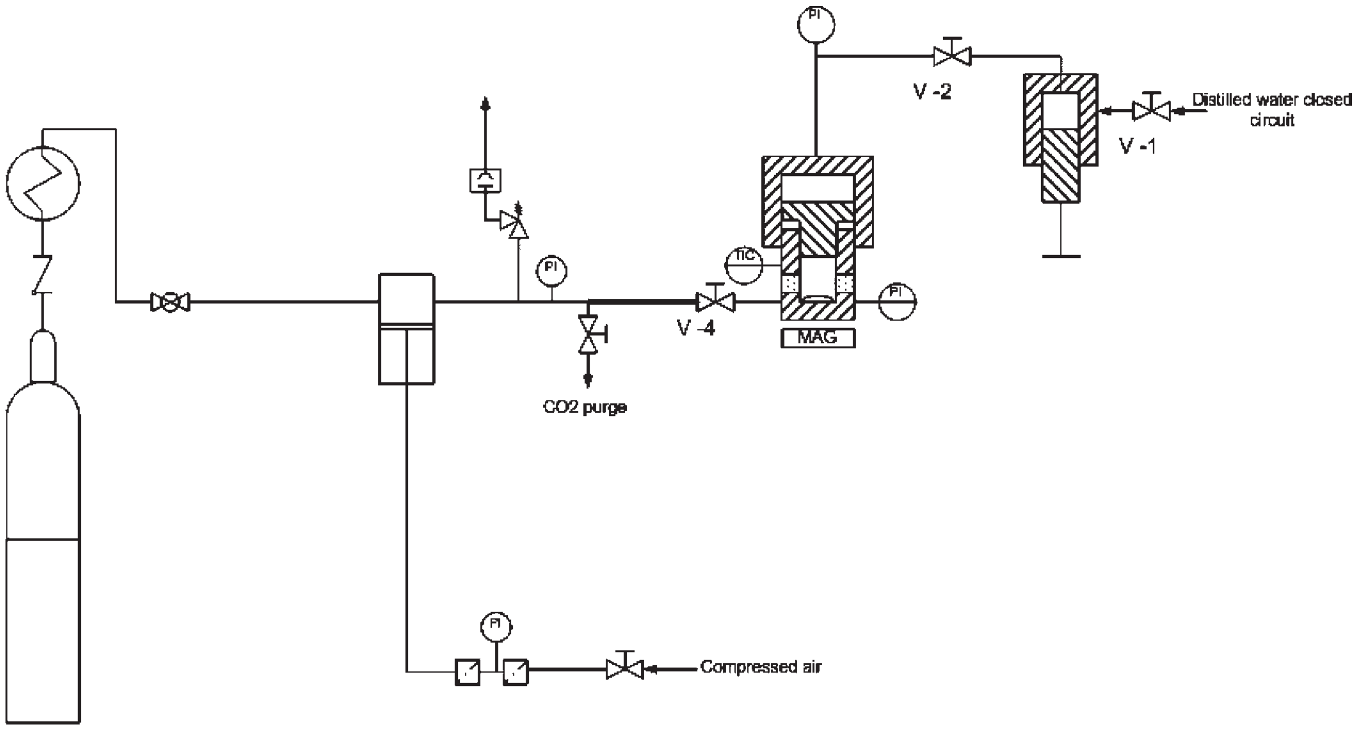

Figure 1. Schematic diagram of the view cell.

(DESIN TPR-18/V2, uncertainty 0.01 MPa). The system also counts with an air-driven pump (MAXIMATOR MO12) used to fill the cell with carbon dioxide. Additional details of the apparatus were provided in a previous work.[11]

Method. The solubility of BPA in SC-CO_2 was measured by visually determining the cloud-point pressure at a fixed temperature and sample composition, according to the synthetic method. For this, the cell was first flushed with CO_2 to remove air, and a known amount of BPA, weighed with an analytical balance (uncertainty: 0.0001 g), was introduced in the visual cell. Afterward, CO_2 was introduced in the cell with the aid of the air-driven pump, until a pressure of approximately 10 MPa. Then, the stirring and the electrical jacket were connected to achieve a homogeneous mixture at the desired temperature. Once that the operating temperature was achieved and remained stable, the density of CO_2 at the pressure and temperature conditions in the cell was calculated using the reference equation of state of Span and Wagner[12] as implemented in the National Institute of Standards and Technology (NIST) chemistry webbok,[13] assuming that the BPA present in the fluid mixture (with a mole fraction concentration of the order of 10^{-5}) does not significantly affect the *PVT* properties of CO_2. With this, the amount of CO_2 loaded in the cell was calculated by the multiplication of CO_2 density and cell volume, and the composition of the sample was calculated from the respective amounts of CO_2 and BPA. The uncertainty of this method for the calculation of sample composition was estimated using a standard statistical error propagation analysis as $\pm\ 5\cdot 10^{-6}$ in the mole fraction of BPA.

For the determination of the solubility, the pressure in the cell was slowly increased using the displaceable piston until the solid was completely dissolved and a single phase was visualized. Then, pressure was decreased until the formation of particles was observed. The process was repeated several times to reduce the pressure interval where the phase change was observed and to ensure the reproducibility of the result. More details were provided in a previous work.[11]

Table 1. Solubility of Bisphenol A in SC-CO_2 as a Function of Pressure and Temperature[a]

T/K	P/MPa	$x_{BPA}\cdot 10^5$
313	16.3	2.5
313	16.4	1.8
313	17.2	2.8
313	17.6	3.3
313	17.8	3.9
313	18.0	4.5
313	18.1	3.8
313	19.1	4.9
333	14.3	2.0
333	14.5	3.4
333	14.7	3.9
333	15.0	3.7
333	15.2	5.0
333	15.4	4.5
333	15.4	4.5
333	15.5	5.2
353	13.0	4.0
353	13.1	4.6
353	13.5	4.6
353	13.7	5.0
353	14.6	7.7

[a] Estimated experimental uncertainties are ± 1 K in temperature, ± 0.5 MPa in pressure, and $\pm\ 5\cdot 10^{-6}$ in bisphenol A mole fraction.

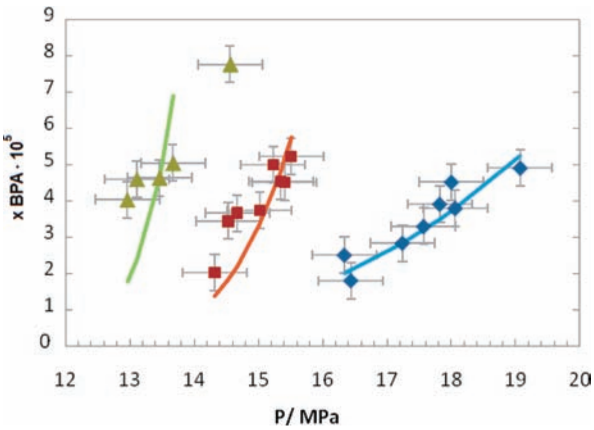

Figure 2. Solubility of bisphenol A in carbon dioxide as a function of pressure and temperature. Symbols: experimental data, ◆, $T = 313$ K; ■, $T = 333$ K; ▲, $T = 353$ K. Solid lines: calculations with the Peng−Robinson equation of state. Error bars indicate the estimated experimental uncertainty.

This visual method allowed determining the equilibrium pressure within a pressure interval of ± 0.5 MPa. During the experiment, the PID temperature controller maintained the temperature in the cell at the set point within ± 1 K. Measurements were carried out in the temperature range 313 K ≤ T ≤ 353 K and pressure range 12 MPa < P < 20 MPa.

RESULTS AND DISCUSSION

The experimental results obtained in this work are presented in Table 1 and Figure 2. As expected, the solubility increased when the pressure was increased. The solubility also increased when temperature was increased, implying that the pressure of measurements is above the crossover point of this system. The mole fraction solubility measured ranged from $1.8 \cdot 10^{-5}$ at $P = 16.3$ MPa and $T = 313$ K to $7.7 \cdot 10^{-5}$ at $P = 14.6$ MPa and $T = 353$ K, corresponding to the mass fraction solubilities of BPA of $9 \cdot 10^{-5}$ and $4 \cdot 10^{-4}$, respectively. As a comparison, the solubility of BPA in SC-CO_2 reported by Margon et al.[9] at higher pressures and temperatures ($P = 30$ MPa and 400 K < T < 480 K) ranged from $2 \cdot 10^{-4}$ to $7 \cdot 10^{-4}$ (mole fraction), which can be considered to be in agreement with the results obtained in this work in terms of the order of magnitude of the solubility as well as its trend of variation with pressure and temperature.

The experimental data obtained were correlated using the Peng−Robinson equation of state with conventional quadratic mixing rules:[14]

$$P = \frac{RT}{v-b} - \frac{a \cdot \alpha(T)}{v(v+b) + b(v-b)} \qquad (1)$$

The solubility of BPA in SC-CO_2 was calculated with this equation by the resolution of the condition of equality of BPA fugacity in the solid and fluid phases:

$$f_{\mathrm{BPA}}^{\mathrm{S}} = f_{\mathrm{BPA}}^{\mathrm{F}} \qquad (2)$$

The fugacity of the solid phase was calculated assuming that it was composed of pure BPA and taking as a reference the fugacity of a subcooled liquid, according to the procedure proposed by Shariati and Peters:[15]

$$f^{\mathrm{S}} = f^{\mathrm{L}} \exp\left(\frac{\Delta H_{\mathrm{f}}}{R}\left(\frac{1}{T_{\mathrm{f}}} - \frac{1}{T}\right)\right) \qquad (3)$$

Table 2. Pure Component Properties

	T_c	P_c		ΔH_f	T_f
	K	MPa	w	kJ·mol^{-1}	K
CO_2	304.2	7.38	0.2252		
bisphenol A	1001.8	3.01	1.379	30.7	429.6

Table 3. Binary Interaction Parameters between Carbon Dioxide and Bisphenol A and Average Absolute Deviations between Experimental Solubility Rata and Calculations with the Peng−Robinson Equation of State at Each Temperature

T/K	k_{ij}	l_{ij}	AAD %
313	0.046	−0.093	9.2%
333	0.120	−0.240	17.3%
353	0.293	−0.585	39.2%

The critical properties of BPA, required for the application of the Peng−Robinson equation, were estimated with the Joback group contribution method,[16] while the temperature and enthalpy of fusion, required for the application of eq 3, were obtained from a DSC analysis of BPA, as described in the Experimental Section. Table 2 summarizes all pure component properties used in calculations with the Peng−Robinson equation of state.

The binary interaction parameters k_{ij} and l_{ij} were obtained by the correlation of the experimental data obtained in this work. The correlation was carried out by a minimization of the average absolute difference AAD % between experimental and calculated BPA solubilities, as defined in eq 4:

$$\mathrm{AAD\%} = \frac{100}{n_{\mathrm{data}}} \sum_{i}^{n_{\mathrm{data}}} \frac{|x_{\mathrm{BPA}}^{\mathrm{exp}} - x_{\mathrm{BPA}}^{\mathrm{calc}}|}{x_{\mathrm{BPA}}^{\mathrm{exp}}} \qquad (4)$$

The binary interaction parameters obtained with this method are reported in Table 3. Temperature-dependent interaction parameters had to be used to obtain an acceptable fit of experimental data, resulting in an average deviation between experimental and calculated solubility data of AAD % = 19 %. Figure 2 presents the results of the calculations of BPA solubility with the Peng−Robinson equation of state together with experimental data. It can be observed that larger deviations between experimental data and model results are observed at 353 K compared to the other two temperatures of measurement, as a consequence of an inaccurate calculation of the slope of the isothermal solubility curve with the equation of state.

CONCLUSIONS

The solubility of bisphenol A in SC-CO_2 has been measured using a view cell according to the synthetic method. The highest solubility observed was $7.7 \cdot 10^{-5}$ (mole fraction) at $P = 14.6$ MPa and $T = 353$ K. Data were correlated using the Peng−Robinson equation of state with two temperature-dependent binary interaction parameters, obtaining an average deviation between experiments and calculations of 19 %.

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LIST OF SYMBOLS

AAD%	average absolute deviation
f	fugacity/MPa
ΔH_f	melting enthalpy/J·mol^{-1}
k_{ij}	binary interaction parameter of Peng–Robinson equation of state
l_{ij}	binary interaction parameter of Peng–Robinson equation of state
P	pressure/MPa
P_c	critical pressure/MPa
R	gas constant/J·mol^{-1}·K^{-1}
T	temperature/K
T_c	critical temperature/K
T_f	melting temperature/K
v	molar volume/m^3·mol^{-1}
w	acentric factor
x	fluid composition, mole fraction

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