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Solubility Studies of Organic Flame Retardants in Supercritical CO_2

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Solubility measurements and calculations were performed for two mainly used flame retardants, for hexabromcyclododecane and for tetrabrombisphenyl-A. For the solubility studies different pressures (200, 300, 400, and 500 bar) and temperatures (25, 40, 60, 80, and 100 °C) were investigated. The experimental data were fitted by means of the Chrastil equation. With this rather simple model the solubility behavior of the solid substances in supercritical carbon dioxide can be described with high accuracy.

Introduction

In the field of polymer recycling and/or disposal (e.g., polymer composites of mass consumer products such as electronic waste), new techniques are highly required. Most of the electronic waste contains flame retardants, mainly halogenated organic substances. In many recycling processes plastics are incinerated and the formation of halogenated dibenzodioxins and dibenzofurans cannot be avoided. One promising way to separate halogenated flame retardants from polymer matrixes is the extraction by supercritical fluids such as supercritical carbon dioxide (SC-CO_2). The advantage of this process is that the polymer as well as the flame retardant can be recycled, especially advantageous because flame retardants are relatively high-priced products.

Before extraction experiments can be started, the solubility behavior has to be known and up to now only little data on flame retardants in combination with supercritical CO_2 are available in the literature.[1,2] For this reason solubility data for the two mainly used flame retardants, for hexabromcyclododecane (HBCD) and for tetrabrombisphenyl-A (TBBA), were performed in a wide range of pressures and temperatures.

Experimental Method

All experiments were carried out in a high-pressure CO_2 apparatus (Speed-SFE from Applied Separations) (see Figure 1) with a 300-mL extractor designed for a maximum pressure of 690 bar and a maximum temperature of 250 °C. The volume of the extractor had to be reduced to 50 mL by a metallic cylinder, which tightens to the extractor wall, because as preliminary tests showed the equilibrium cell has to be completely filled with material. Otherwise, diffusion is the limiting factor and time for reaching equilibrium was too long. The extraction vessel was filled with compressed CO_2 by an air-driven pump at closed outlet valves and under static conditions, which means desired pressure and temperature; the cell was incubated for 15 h, maintaining these conditions to reach equilibrium. In preliminary experiments the equilibrium time of 15 h was determined to reach equilibrium.

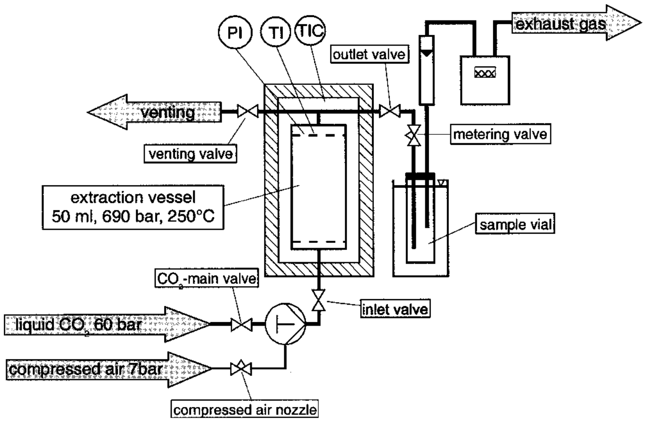

Figure 1. Flow sheet of the high-pressure CO_2 plant.

CO_2 Sampling. At equilibrium a CO_2 phase sample is taken by opening the outlet valve and expanding a certain amount of CO_2−substance mixture into a cooling trap filled with toluene, which has the highest solubility for the measured substances under atmospheric conditions. The pure gaseous CO_2 passes a rotameter, showing the actual flow rate, and a gas flowmeter for determining the expanded CO_2 amount. The content of the cooling trap was filled up with toluene to 30 mL and analyzed by a gas chromatographic method using an electron capture detector (GC-ECD). With the mass of expanded CO_2 and composition of the cooling trap solubility at a certain pressure and temperature was calculated. Sampling was repeated four times at a given pressure and temperature and the standard deviation was lower than 5%.

Gas Chromatographic Method. The toluene−flame retardant mixture of CO_2 sampling was analyzed in a gas chromatograph (HP 5890 Serie II) with an ECD using a capillary column (type HP-1, 12 m × 0.2 mm × 0.2 μm). The injector temperature was held constant at 290 °C and the detector temperature at 300 °C. The oven temperature was held constant at 290 °C. Calibration with different amounts of HBCD and TBBA in toluene has been done before determining the linear range of calibration line and retention time of substances.

CO_2 Density Calculations. The density of pure CO_2, depending on pressure and temperature, was calculated

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Table 1. Solubility of HBCD in CO_2 (wt %)

	pressure			
temperature	200 bar	300 bar	400 bar	500 bar
25 °C	0.053	0.060	0.068	0.076
40 °C	0.056	0.066	0.101	0.169
60 °C	0.052	0.108	0.190	0.293
80 °C	0.043	0.153	0.335	0.579
100 °C	0.054	0.266	0.513	0.803

Table 2. Solubility of TBBA in CO_2 (wt %)

	pressure			
temperature	200 bar	300 bar	400 bar	500 bar
25 °C	0.019	0.021	0.026	0.031
40 °C	0.045	0.061	0.076	0.092
60 °C	0.028	0.058	0.090	0.122
80 °C	0.022	0.085	0.159	0.231
100 °C	0.032	0.133	0.249	0.432

with the equation of Bender,[3,4]

$$p = RT\rho + B\rho^2 + C\rho^3 + D\rho^4 + E\rho^5 + F\rho^6 + (G + H\rho^2)\rho^3 \exp(-a_{20}\rho^2) \quad (1)$$

with

$$B = a_1T - a_2 - \frac{a_3}{T} - \frac{a_4}{T^2} - \frac{a_5}{T^3}$$

$$\mathrm{C} = \mathrm{a}_5\mathrm{T} + \mathrm{a}_7 + \frac{\mathrm{a}_8}{\mathrm{T}}$$

$$D = a_9T + a_{10}$$

$$E = a_{11}T + a_{12}$$

$$F = a_{13}$$

$$G = \frac{a_{14}}{T^2} + \frac{a_{15}}{T_3} + \frac{a_{16}}{T^4}$$

$$H = \frac{a_{17}}{T^2} + \frac{a_{18}}{T_3} + \frac{a_{19}}{T^4}$$

By this way the weight of CO_2 passing the gas flowmeter was calculated along with the CO_2 density in the equilibrium cell at given pressure and temperature.

Materials

Hexabromcyclododecane (HBCD) with a purity of 97% was purchased by Sigma Aldrich and tetrabrombisphenyl-A (TBBA) with a purity of 98% by Riedel de Haen. To remove the impurities of both substances, which may influence solubility data, they were extracted with CO_2 (400 bar, 60 °C, 12-h extraction time) and analyzed by GC-ECD before using for solubility tests. Toluene (purity >99.8%) was purchased by Merck. The carbon dioxide with a purity >99.94% and a dew point lower than −60 °C was purchased by Linde (Graz) and stored in a tank with 3200-L capacity.

Results

Table 1 shows our original, unsmoothed data for the HBCD−CO_2 system and in Table 2 the data for the TBBA−CO_2 system at 25, 40, 60, 80, and 100 °C are depicted.

No critical parameters are available for HBCD and TBBA and the methods for calculating these data give too different results so that no fugacity calculation using cubic equations of state could be done. Therefore, the experimental data were fitted by the Chrastil [5] equation as given in eq 2, where no specific data of the pure substances are necessary,

$$\ln c = k \ln \rho + \frac{a}{T} + b \qquad (2)$$

where c is the concentration (g/L of CO_2 at actual pressure and temperature conditions), ρ is the CO_2 density (g/L), T is the temperature (K), and a, b, and k are the fitting parameters. In our case we did not determine the parameters a and b separately, but we calculated the parameter d, which includes a and b. Further, we assumed that parameter k is temperature dependent so we used the following form:

$$\ln c = k(T) \ln \rho + d(T) \qquad (3)$$

The $k(T)$ and $d(T)$ values for HBCD in CO_2 are fitted by the following equations:

$$k(T) = -0.0000793T^3 + 0.0800975T^2 - 26.92107181T + 3021.2374228 \quad (4)$$

$$d(T) = 0.0005251T^3 - 0.5301042T^2 + 178.2306307T - 20016.08243406 \quad (5)$$

A comparison of the experimental data and eqs 3−5 fitted solubility data of HBCD is given in Figure 2.

The equations for fitting $k(T)$ and $d(T)$ for TBBA in CO_2 are

$$k(T) = 0.0000248T^3 - 0.0266704T^2 + 9.5473647T - 1130.254909 \quad (6)$$

$$d(T) = -\,0.0001804T^3 + 0.1938425T^2 - 69.2613482\mathrm{T} + 8182.688507 \quad (7)$$

A comparison of the experimental data and eqs 3, 6, and 7 fitted solubility data of TBBA is given in Figure 3.

The comparison of experimental data and the Chrastil equation calculated data shows that this model describes the solubility behavior of the solid substances HBCD and TBBA in supercritical CO_2 very well. In Table 3 the average relative error Δ%, calculated by eq 8, is given for solubilities of HBCD and TBBA at the different temperature sets. The solubility data at 25 °C could not be fitted as a result of totally different values for $k(T)$ and $d(T)$ that arise because of the liquid state of CO_2 at this temperature and therefore different density behavior than that at supercritical temperatures:

$$\Delta\% = \frac{100}{n}\sum_{n=i}^{n}\frac{y_i^{\mathrm{calc}} - y_i^{\mathrm{exp}}}{y_i^{\mathrm{exp}}} \qquad (8)$$

These solubility data are the basic data for following extraction tests and it is obvious that for high extraction yields the upper region of pressure and temperature will be successful because higher solubility of HBCD as well

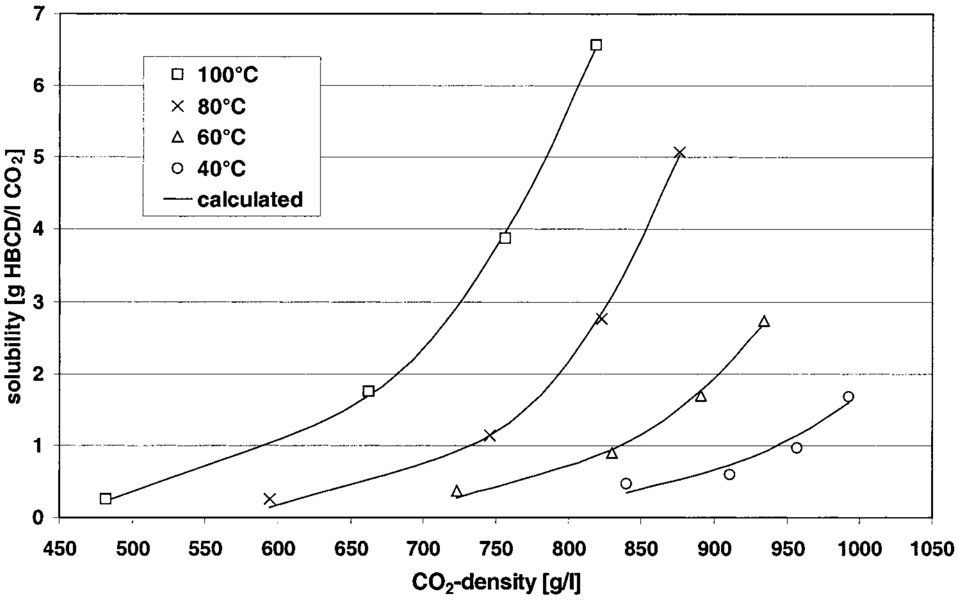

Figure 2. Experimental and calculated solubility data of HBCD in CO$_2$.

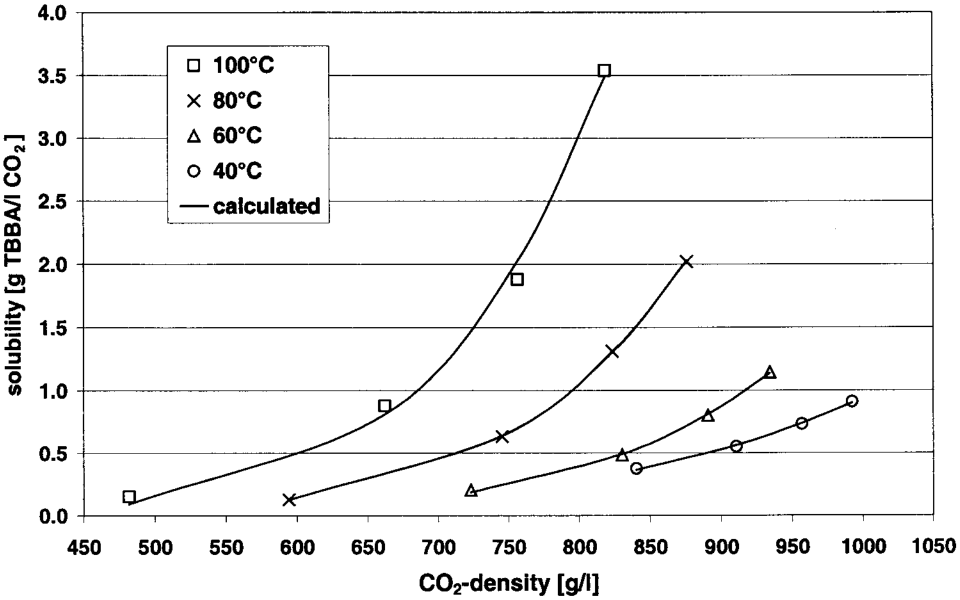

Figure 3. Experimental and calculated solubility data for TBBA in CO$_2$.

Table 3. Average Relative Error Δ% for HBCD and TBBA

	HBCD	TBBA
40 °C	1.536	−0.217
60 °C	−4.430	−1.431
80 °C	−10.518	−0.186
100 °C	−3.767	−10.710
total	−4.295	−3.136

as TBBA in supercritical CO$_2$ can be achieved and therefore lower CO$_2$ mass flow will be necessary. Economic aspects for this process can be done after performing extraction tests because besides solubility different parameters such as particle size, flow rate of CO$_2$, or CO$_2$ velocity in the extractor influence extraction yields.

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