Solubility of Triphenylmethyl Chloride and Triphenyltin Chloride in Supercritical Carbon Dioxide

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The solubility of triphenyltin chloride (TPT) and triphenylmethyl chloride (TPC) in supercritical carbon dioxide (SC-CO_2) was measured with a dynamic method at temperatures from 308.15 K to 338.15 K and pressures ranging from 15 MPa to 40 MPa. The two compounds displayed a similar mole fraction solubility in SC-CO_2 of about 10^{-3} to 10^{-4} with a relative uncertainty of about 6 % over the range of experimental conditions. The experimental solubility data were correlated with both empirical Gordillo and semiempirical Chrastil models. The correlation results indicated that the values of average relative deviations (ARD) with the Gordillo model for TPT and TPC were 5 % and 12 %, and those of with the Chrastil model were 9 % and 6 % respectively.

Introduction

Organotin compounds (OTCs) are widely used in antifouling painting, which has been an important pollution in the marine environment.[1] The sea products contaminated by the OTCs are a problem in food safety. So a need exists for a rapid, sensitive, and accurate method to determine the levels of OTCs, including triphenyltin chloride [TPT, $(C_6H_5)_3SnCl$], in sea products.

Supercritical fluid extraction (SFE), which is considered an environmentally friendly and highly effective technology, is now being evaluated as a possible alternative approach for analyzing harmful chemical residues in biological samples.[2] In our laboratory, supercritical CO_2 (SC-CO_2) extraction has been studied as a competitive pretreatment method for determination of OTCs. It is necessary to know the solubility of TPT in SC-CO_2 initially in order to develop a SFE process for the determination of OTCs in environment samples.[3,4] In addition, as the molecular structure of triphenylmethyl chloride [TPC, $(C_6H_5)_3CCl$] is similar to that of TPT, the solubility of TPC in CO_2 was also studied for comparison with that of TPT. To our best knowledge, no solubility data for TPT and TPC in SC-CO_2 have been reported in the literature.

Additionally, the empirical models of Gordillo and the semiempirical models of Chrastil are used to make the measured solubility data correlation respectively in this paper.

Experimental Section

Materials. Triphenyltin chloride (CAS No. 639-58-7, 99 % purity) and triphenylmethyl chloride (CAS No. 76-83-5, 99 % purity) were purchased from Sigma-Aldrich. Food-grade carbon dioxide (> 99.95 %) was obtained from Beijing Ap Beifen Gases Industry (Beijing, China). Ethanol (HPLC grade) was supplied by Tianjin Chemical Reagent Factory (Tianjin, China). All chemicals were used without further purification.

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Table 1. Comparison of Solubility of Benzoic Acid in SC-CO_2 with Literature Values: Pressure, p; Temperature, T; SC-CO_2 Density, ρ; Mole Fraction Solubility, y; and Mole Fraction Solubility in the Literature,[6,7] y^{ref}

T / K	p / MPa	10^3y	10^3y^{ref}	RD / %
318.15	16.0	2.40	2.37	1.3
318.15	20.0	3.23	3.18	1.6
318.15	24.0	4.20	4.21	0.2
318.15	28.0	4.39	4.38	0.2
308.15	16.0	2.17	2.19	0.9
308.15	20.0	2.66	2.53	4.9
308.15	24.0	2.87	2.81	2.1
308.15	28.0	3.02	3.03	0.3

Experimental Apparatus and Procedure. The solubility measurements were performed with a modified Spe-ed SFE instrument (Applied Separations Inc., Allenton, PA). The apparatus and procedure were described in the literature.[5] During the solubility measurement, the pressure fluctuation was within ± 0.05 MPa, and the temperature fluctuation was controlled within ± 0.02 K. The solubility was obtained gravimetrically.

Results and Discussion

Apparatus Reliability Test. The reliability of the apparatus was checked by measuring the mole fraction solubility (y) of benzoic acid in supercritical carbon dioxide at 308.15 K and 318.15 K. The results are listed in Table 1. The solubility data obtained are in fair agreement with those reported in the literature[6,7] with relative deviations (RD) of less than 5 %.

Solubility Data. The solubility data for TPT and TPC in SC-CO_2 at different temperatures ranging from 308.15 K to 338.15 K and pressures ranging from 15 MPa to 40 MPa are listed individually in Tables 2 and 3. Each solubility data point is the average of three experimental measurements and the relative standard deviation (RSD) for TPT and TPC were within ± 6 % and ± 8 %, separately. In addition, the measured concentration of solutes was converted to mole fraction based on the IUPAC International Thermodynamic Tables for the density of SC-CO_2.[8]

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Table 2. Solubility of Triphenyltin Chloride in SC-CO_2: Pressure, p; Temperature, T; SC-CO_2 Density, ρ; Mass Fraction Solubility, s ($g \cdot L^{-1}$), Mole Fraction Solubility, y; Mole Fraction Solubility Calculated by the Gordillo Equation, y^{cal}; Solubility Calculated by the Chrastil Equation, s^{cal} ($g \cdot L^{-1}$)

T	p	ρ				
K	MPa	$g \cdot L^{-1}$	$10^4 y$	$10^4 y^{cal}$	$10^2 s$	$10^2 s^{cal}$
308.15	15.0	815.0	4.12	4.13	0.71	0.67
	20.0	866.1	4.90	4.96	0.84	0.84
	25.0	901.7	5.30	5.48	0.91	0.97
	30.0	929.6	5.83	5.55	1.00	1.08
318.15	15.0	742.4	3.62	3.52	0.62	0.64
	20.0	813.3	5.31	4.97	0.91	0.68
	25.0	857.9	5.96	6.47	1.03	1.16
	30.0	891.0	7.65	7.74	1.32	1.34
328.15	15.0	653.8	2.71	2.96	0.47	0.54
	20.0	755.0	5.64	4.94	0.97	0.97
	25.0	811.2	7.06	7.58	1.21	1.31
	30.0	850.9	10.96	10.69	1.89	1.59

Table 3. Solubility of Triphenylmethyl Chloride in SC-CO_2: Pressure, p; Temperature, T; SC-CO_2 Density, ρ; Mass Fraction Solubility, s ($g \cdot L^{-1}$); Mole Fraction Solubility, y; Mole Fraction Solubility Calculated by the Gordillo Equation, y^{cal}; Solubility Calculated by the Chrastil Equation, s^{cal} ($g \cdot L^{-1}$)

T	p	ρ				
K	MPa	$g \cdot L^{-1}$	$10^4 y$	$10^4 y^{cal}$	$10^2 s$	$10^2 s^{cal}$
308.15	15.0	815.0	3.82	3.67	0.48	0.50
	20.0	866.1	6.25	5.54	0.78	0.66
	25.0	901.7	6.68	7.30	0.83	0.80
	30.0	929.6	7.23	8.41	0.90	0.91
	35.0	952.8	7.57	8.48	0.94	1.02
	40.0	972.8	9.07	7.48	1.13	1.20
323.15	15.0	698.1	3.64	4.06	0.45	0.50
	20.0	784.2	8.35	6.93	1.04	0.92
	25.0	834.6	10.40	10.33	1.30	1.26
	30.0	871.0	12.70	13.47	1.58	1.56
	35.0	899.9	13.90	15.37	1.73	1.83
	40.0	924.0	16.50	15.33	2.05	2.07
338.15	15.0	555.5	2.93	3.91	0.36	0.41
	20.0	692.3	10.40	7.54	1.30	1.05
	25.0	762.4	13.80	12.72	1.72	1.71
	30.0	809.5	18.60	18.78	2.32	2.33
	35.0	845.2	21.90	24.24	2.73	2.91
	40.0	877.3	27.00	27.36	3.36	3.44

As the Gordillo equation and Chrastil model are used for data correlation, both calculated solubility values and experimental values of y (mole fraction) and s ($g \cdot L^{-1}$) are listed in the Tables 2 and 3.

The experimental data listed in Tables 2 and 3 indicate that the mole fraction solubility of TPT and TPC in SC-CO_2 increases with increasing pressure at constant temperature and they are on the same order of magnitude of 10^{-4} to 10^{-3} under the experimental conditions employed. The similar solubility of TPT and TPC in CO_2 may be explained in terms of intermolecular forces. Since the central atom of Sn in TPT is replaced by a C atom in TPC, the molecular weight and boil temperature of TPT is a little higher than that of TPC. As a result, the solubility of TPT is a little lower than that of TPC.

Data Correlation. Experimental data of the solubility of TPT and TPC were correlated by the Gordillo and Chrastil models. The average relative deviation (ARD) was used to test the correlation accuracy, which is defined as

$$\mathrm{ARD} = \frac{1}{N}\sum_{N}\frac{|y^{cal} - y|}{y} \quad (1)$$

where N is the number of data points and y^{cal} and y are the calculated mole fraction solubility values and the experimental mole fraction solubility data, respectively. When the Chrastil model was used, the y^{cal} and y should be replaced by the calculated and measured solubility value of s. The lower the value of the ARD, the better the correlation results.

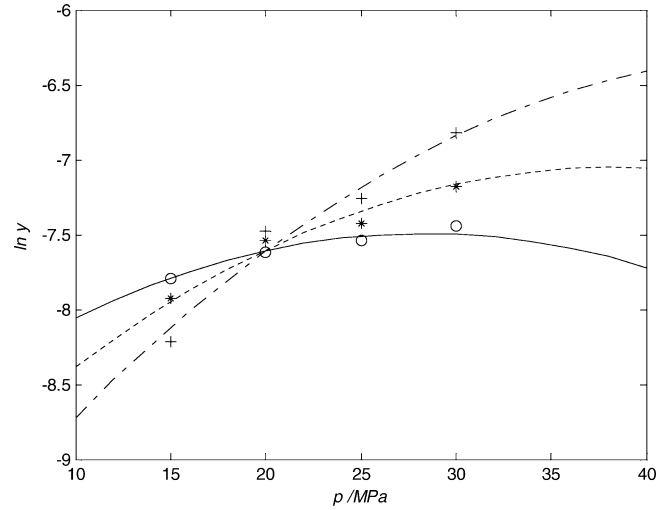

Figure 1. The correlation results of experimental solubility values for triphenyltin chloride by the Gordillo equation: ○, —, 308.15 K; *, - - -, 318.15 K; +, — - —, 328.15 K.

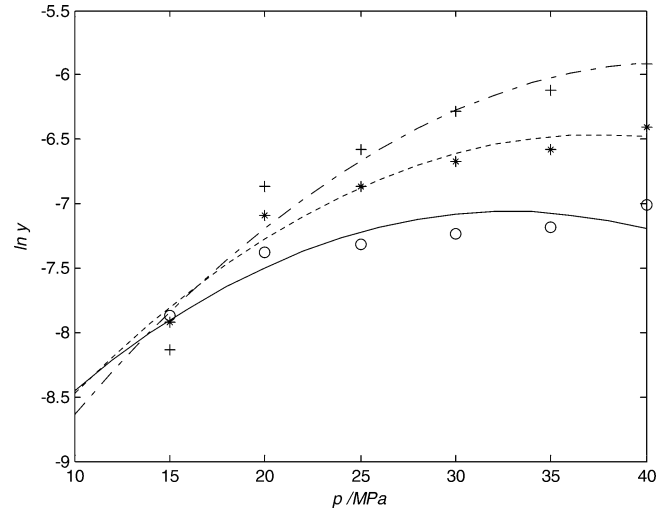

Figure 2. The correlation results of experimental solubility values for triphenylmethyl chloride by the Gordillo equation: ○, —, 308.15 K; *, - - -, 323.15 K; +, — - —, 338.15 K.

The Gordillo model is an empirical model that considered the influence of temperature and pressure on the density of SCF.[9] The Gordillo equation is

$$\ln y = D_0 + D_1 P + D_2 P^2 + D_3 PT + D_4 T + D_5 T^2 \quad (2)$$

where y is the mole fraction solubility of solute in SC-CO_2 and D_0 to D_5 are the regression constants. These regression constants are obtained by performing a multiple linear regression on the experimental data.

The experimental data of TPT and TPC are correlated by the Gordillo model, as shown in Figures 1 and 2, respectively. The regression constants D_0 to D_5 for TPT are as follows: $D_0 = 6.4$, $D_1 = -0.92$, $D_2 = -1.7 \cdot 10^{-3}$, $D_3 = 3.3 \cdot 10^{-3}$, $D_4 = -3.4 \cdot 10^{-2}$, $D_5 = -5.0 \cdot 10^{-5}$. The regression constants for TPC are as follows: $D_0 = -35$, $D_1 = -0.33$, $D_2 = -4.9 \cdot 10^{-3}$, $D_3 = -2.7 \cdot 10^{-3}$, $D_4 = 0.18$, $D_5 = 3.1 \cdot 10^{-4}$. The ARD of the fitted Gordillo model for TPT was calculated to be 5 %, and that for TPC was 12 %.

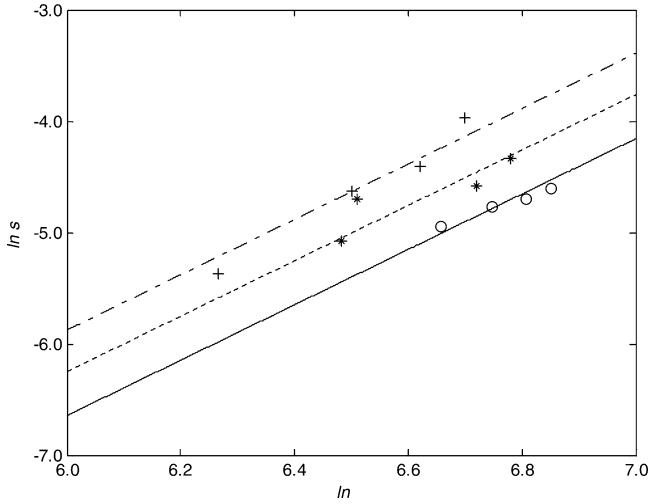

Figure 3. The correlation results of experimental solubility values for triphenyltin chloride by the Chrastil equation: ○, —, 308.15 K; *, - - -, 318.15 K; +,— - —, 328.15 K.

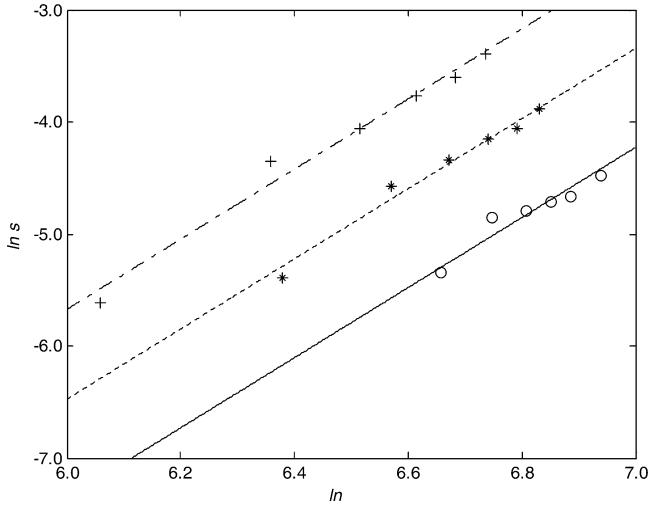

Figure 4. The correlation results of experimental solubility values for triphenylmethyl chloride by the Chrastil equation: ○, —, 308.15 K; *, - - -, 323.15 K; +,— - —, 338.15 K.

The Chrastil model gives a macroscopic description of the number of molecules surrounding the solute in the fluid phase.[10] It is based on the hypothesis that one molecule of a solute A (i.e., TPT) associates with k molecules of a solvent, B (i.e., CO_2), to form one molecule of a solute−solvent complex, AB_k, which is in equilibrium with the fluid. The Chrastil equation is

$$\ln s = \mathrm{k} \ln \rho + \frac{\alpha}{T} + \beta \qquad (3)$$

where s is the solute solubility in SC-CO_2, k is the association number, and ρ is the SC-CO_2 density. The parameters, k, α, and β are constants that can be obtained by performing a multiple linear regression on the experimental data.

The correlation results of TPT and TPC with the Chrastil model are represented in Figures 3 and 4, respectively. By performing a multiple linear regression on ln s as a function of ln ρ and $1/T$, the parameters ware obtained; i.e., $k = 2.5$, $\alpha = -3800$ K, $\beta = -9.0$ for TPT, and $k = 3.1$, $\alpha = -5800$ K, $\beta = -7.2$ for TPC. The ARD values of the fitted Chrastil model for TPT and TPC were calculated to be 9 % and 6 %, respectively.

Conclusions

The solubility of triphenyltin chloride and triphenylmethyl chloride in supercritical carbon dioxide was measured with a dynamic method at temperatures from 308.15 K to 338.15 K and pressures of 15 MPa to 40 MPa. Their mole fraction solubility values in SC-CO_2 are from 10^{-3} to 10^{-4} over the range of experimental conditions. Experimental solubility data of TPT and TPC were correlated by the Gordillo and Chrastil models, and good fits were obtained.

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