Solubility of Chlorinated Pesticides in Supercritical Carbon Dioxide

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Supercritical fluid extraction is a potential technique for the decontamination of soils and other solid materials containing residual pesticides. The solubilities of pesticides in supercritical carbon dioxide are being measured as part of a program in which this extraction technology is being investigated. The solubilities of methoxychlor, endrin, and lindane in supercritical CO_2, as measured using a dynamic saturation technique, are reported at pressures between 100 and 220 bar and at two temperatures, 313.1 and 331.1 K. These chemicals have relatively high solubilities with the measured values ranging from 7.36×10^{-6} to 2.69×10^{-3} mole fraction. The solubilities exhibit a clear dependence on the solvent density, and this has been used to provide a simple and precise correlation of the data.

Introduction

Supercritical fluid extraction (SFE) can offer solutions to difficult environmental separations such as the removal of toxic and nonvolatile pollutants from soils and other substrates. A significant advantage of SFE in the handling of pollutants is that there are no potentially toxic emissions from the treatment plant and the solvent (usually a gas at ambient conditions) will not be contaminated with the extract. Several environmentally based applications of SFE technology have been proposed including the regeneration of activated carbon, soil remediation, and cleanup of aqueous waste streams (Groves et al., 1985; Akgerman et al., 1991).

The solubility of the pollutant species in the supercritical fluid is a very important property that is significant in defining the performance of an extraction. One difficulty that is encountered in the evaluation of this type of extraction is that the pollutant molecules are often irregular and complex in structure and there are usually very few physical and chemical property data known about them. Existing techniques for estimating these properties such as group contribution methods are not normally reliable for irregular molecules. Pesticides and herbicides fall into this category, and therefore the solubilities of three pesticides—methoxychlor (1,1-bis(4-methoxyphenyl)-2,2,2-trichloroethane), lindane (γ-1,2,3,4,5,6-hexachlorocyclohexane), and endrin (1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,-4a,5,6,7,8,8a-octahydro-*endo*,*endo*-1,4:5,8-dimethanonaphthalene)—have been measured in supercritical CO_2.

Experimental Section

Apparatus and Procedures. The solubilities of the three pesticides in pure CO_2 were measured using a continuous flow apparatus similar to that described previously (Yun et al., 1991; Gurdial and Foster, 1991; Macnaughton and Foster, 1994) and as shown schematically in Figure 1.

Liquid carbon dioxide (food grade, 99.8% minimum purity) was fed through a 2-μm filter to an ISCO 260D high-pressure syringe pump. The CO_2 was compressed and pumped into a preheating coil contained in a temperature-controlled water bath. Thermal equilibrium was achieved in the preheating coil, and the fluid then passed into an equilibrium cell packed with solute and plugged at each end with glass wool to eliminate entrainment. The solute laden CO_2 leaving the cells was directed through a 0.5-μm filter to prevent physical entrainment. The fluid was then flashed to atmospheric pressure through a regulating valve resulting in the precipitation of solute within both the valve and a 0.5-μm filter attached immediately downstream of the valve. The gas released through the regulating valve was passed through a water saturator and a wet test meter for volume determination.

During each experiment the system pressure was maintained to within ±0.2% of the desired value by adjusting the regulating valve and the pump flow rate. The system temperature was controlled to within ±0.1 K using an immersion circulator (Haake N3). The determination of solubility was based on the mass of solute trapped in a valve and filter and the corresponding volume of CO_2. The gas volume was measured with a precision of 0.01 L using a wet test meter (SIM Brunt) that was calibrated to an accuracy of ±0.4%. The mass of solute was determined to ±0.2 mg using a Mettler H31 balance. The typical mass of solute that was collected in each experiment was greater than 100 mg, giving a potential error due to weighing of 0.2%. The system temperature was measured using an RTD platinum probe accurate to ±0.1 K, and the system pressure was measured using a Druck pressure transducer (DPI 260) accurate to ±0.1%.

The reliability and efficiency of this solubility measuring technique have been previously established by measuring the solubility of naphthalene in CO_2 and comparing the data with those of Tsekhanskaya et al. (1964) (Gurdial, 1991). In this study, a new experimental apparatus was constructed at the University of Trieste and the reliability of this apparatus was determined by measuring the solubility of salicylic acid in supercritical CO_2. Several solubility data have been reported for the salicylic acid + CO_2 system, and the magnitude of the solubility (10^{-4} mole fraction) is more relevant to the systems being investigated in this study compared with naphthalene, which has a very high solubility in CO_2. The solubility of salicylic acid was measured at 313.1 K, and the results are shown in Figure 2. With the exception of the data around 150–200 bar there is excellent agreement with the data of Gurdial and

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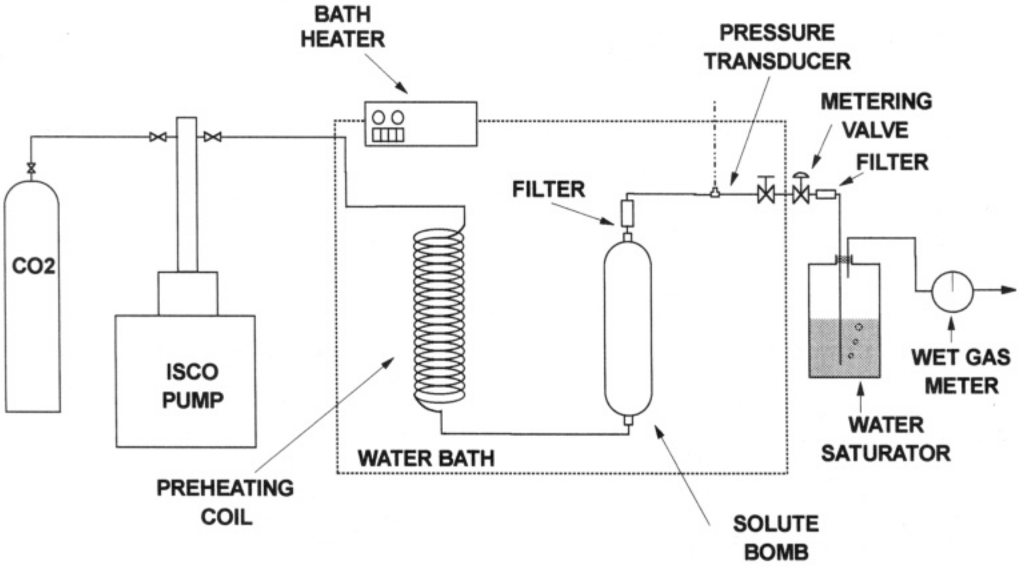

Figure 1. Experimental apparatus.

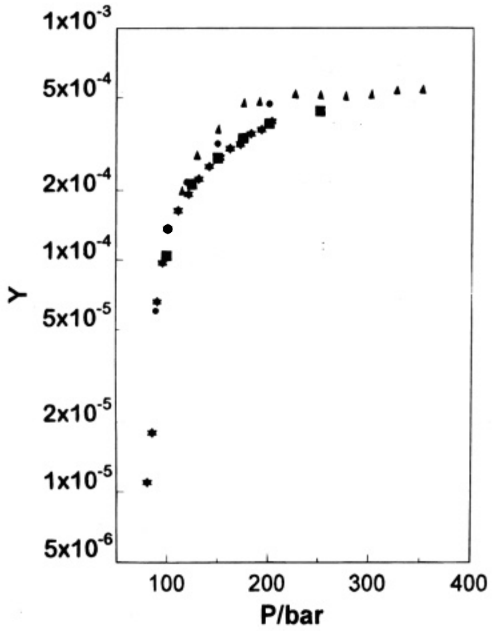

Figure 2. Solubility of salicilic acid y as a parameter of pressure P in supercritical carbon dioxide. (▲) Reverchon et al. (1994); (■) this study; (★) Gurdial and Foster (1991); (●) Stahl et al. (1978).

Table 1. Source and Purity of Materials Used

material	source	purity (%)
CO_2	SIAD	99.98
methoxychlor	Aldrich	95
lindane	Aldrich	97
endrin	Pinus d.d, Slovenia	95% (technical grade)
salicyclic acid	Fluka	99.5

Foster (1991), Stahl et al. (1978), and Reverchon et al. (1994). At these intermediate pressures, at which crossover phenomena are present (Reverchon et al., 1994), there is a discrepancy of up to 20% among the published data.

Materials. The sources and purities of the chemicals used in this study are listed in Table 1. The pesticides were not purified before use; however, in the process of measuring the solubilities small quantities of volatile impurities were extracted. These impurities appeared in the extract as viscous liquids and were only present during the extraction of the first 2−4% of the material charged in the extraction vessel. Solubility measurements were only commenced after there was no longer any evidence of impurities in the extract. The extractions on which the measurements were based yielded homogeneous and uniformly colored crystals.

Table 2. Experimental Solubility for the Pesticides in Supercritical CO_2

			10^4y		
T/K	P/bar	$\varrho(CO_2)$/kg m^{-3}	endrin	methoxychlor	lindane
313.1	100	630.0	3.40	1.64	5.44
	130	743.6	7.69	3.92	10.4
	160	795.6	10.9	6.03	14.2
	190	830.9	14.6	7.37	17.2
	220	858.1	16.4	9.58	19.6
333.1	100	289.8	0.179	0.074	0.507
	130	506.7	2.59	1.41	5.10
	160	637.8	8.06	4.87	13.2
	190	707.0	13.7	9.25	21.4
	220	752.9	19.1	14.2	26.9

Results

The solubilities of the three pesticides are listed in Table 2 along with the temperature, pressure, and density of CO_2 (Angus et al., 1976) that corresponded to each measurement. The results listed in Table 2 represent the average of three separate experimental measurements. The maximum deviation among the three measurements was 3%. This deviation of 3% gives a good indication of the expected accuracy of the results because the individual equipment errors that contribute to the overall error (i.e. pressure, temperature, mass, and volume) are all significantly below this level. Three percent variation is due to random experimental errors associated with the difficulties of working with high-pressure supercritical fluids and inherent problems with the continuous flow technique used, such as partial clogging of the regulating valve with consequently possible fluctuations of flow rate.

The solubilities for each system as a function of pressure are given in Figures 3−5. These results show trends that are similar to those of previous studies (Macnaughton and Foster, 1994; Foster et al., 1991). The crossover pressure is clearly defined where the two isotherms intersect (en-

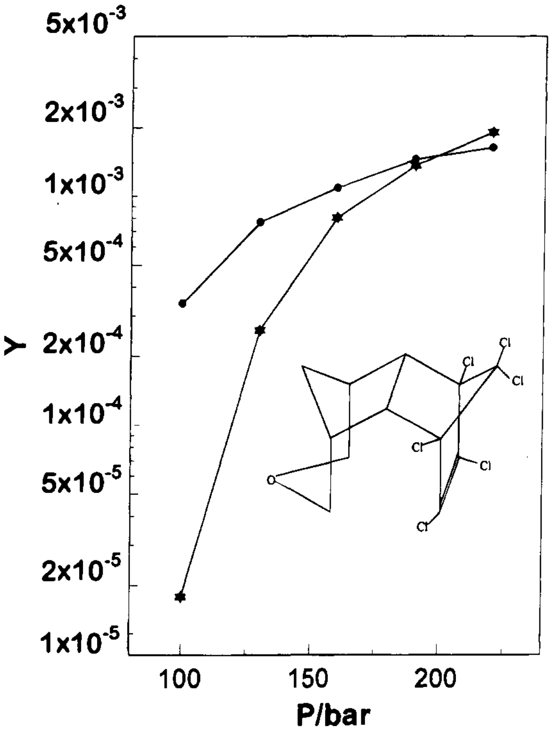

Figure 3. Solubility of endrin y as a parameter of pressure P in supercritical carbon dioxide at 313.1 (●) and 333.1 K (★).

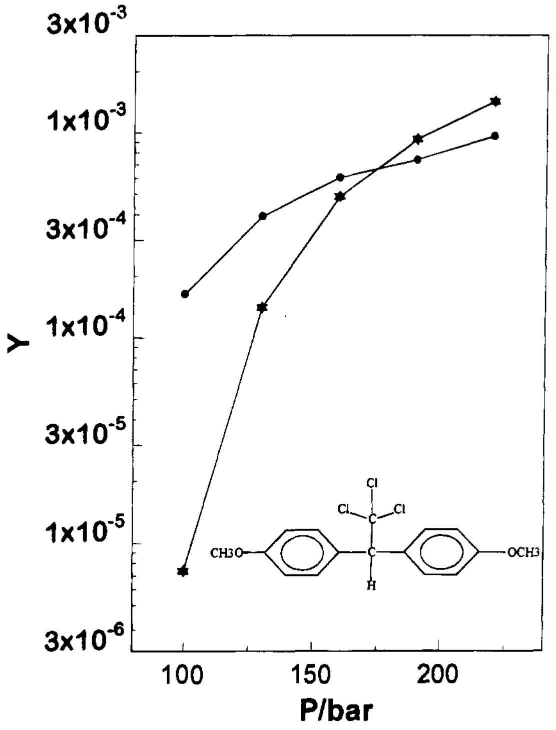

Figure 4. Solubility of methoxychlor y as a parameter of pressure P in supercritical carbon dioxide at 313.1 (●) and 333.1 K (★).

drin, 200 bar; methoxychlor, 175 bar; and lindane, 170 bar). Below this pressure, the solubility decreases with increases in temperature, and above this value, the reverse is the case. Supercritical solubility is strongly influenced by the system temperature and the density of the solvent. The influences of these two variables are shown in Figure 6, which presents the solubility of lindane as a function of CO_2 density. The isothermal dependence of solubility on density can be clearly seen. The solubility also increases with isochoric increases in temperature due primarily to the associated increase in vapor pressure.

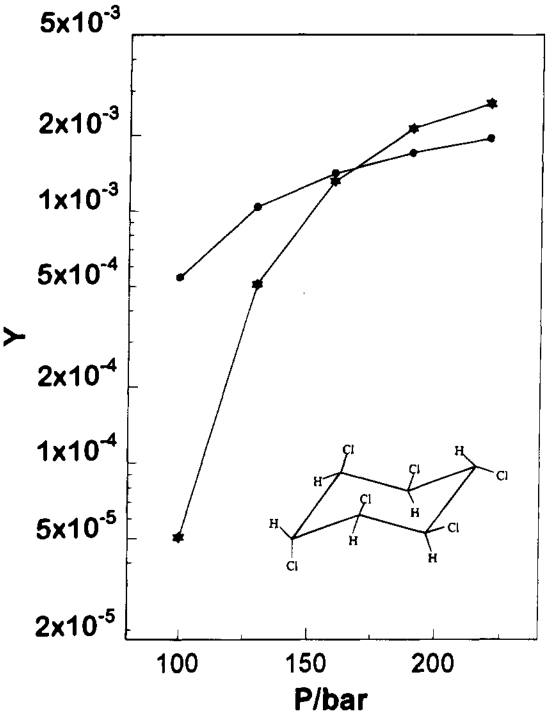

Figure 5. Solubility of lindane y as a parameter of pressure P in supercritical carbon dioxide at 313.1 (●) and 333.1 K (★).

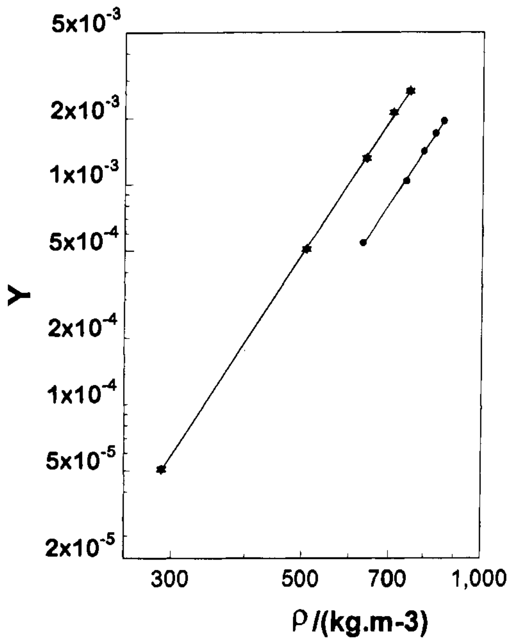

Figure 6. Solubility of lindane y in supercritical carbon dioxide as a function of the carbon dioxide density ρ at 313.1 (●) and 333.1 K (★). Lines represent regression fit of the data.

Discussion

There is a significant lack of physical and chemical property data for the pesticides used in this study. The available data are listed in Table 3. The solubilities of the pesticides at 313.1 K are shown in Figure 7 as a function of density. The solubility of DDT (Macnaughton and Foster, 1994) has been included for comparison purposes. Methoxychlor and DDT have very similar solubilities,

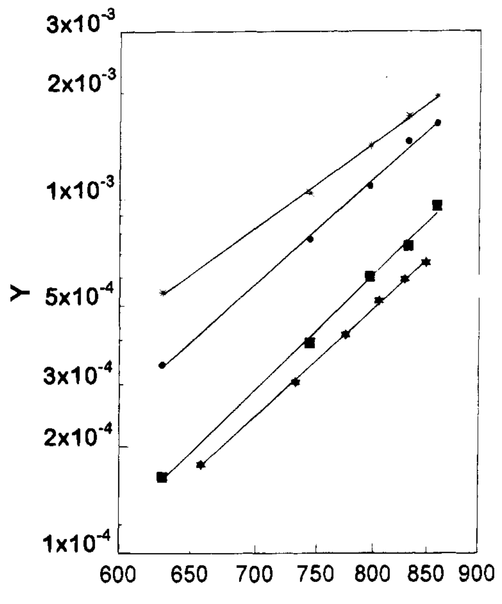

Figure 7. Solubility of four pesticides in supercritical carbon dioxide as a function of carbon dioxide density ϱ at 313.1 K: (●) endrin; (■) methoxychlor; (★) DDT; (*) lindane.

Table 3. Melting Point t_m, Vapor Pressure *P*, and Molar Mass *M* for the Pesticides (Worthing, 1991)

pesticide	t_m/°C	*P*/mPa	*M*
methoxychlor	89	no data	345.65
endrin	226	0.027 (25 °C)	380.93
lindane	112–113	5.6 (20 °C)	290.85
DDT	108.5–109	0.025 (20 °C)	354.51

which reflects their structural similarities. The only difference in structure between the two molecules is that the methoxy groups on methoxychlor are replaced by chlorine atoms in DDT. The solubilities of lindane and endrin are also similar, perhaps reflecting the very high chlorine substitution of each molecule. Although the vapor pressure of lindane is considerably higher than that of endrin, this is not strongly reflected in their solubilities.

Modeling of solubility is difficult due to almost complete lack of knowledge of the physical properties for these compounds and the general unreliability of estimation methods for irregular molecules. For example, to model the data using the Peng–Robinson equation of state, the critical temperature and pressure, the accentric factor, the vapor pressure, and the molar volume of each pesticide are required. In a previous study Macnaughton and Foster (1994) used a combination of property estimation and an empirical modification to the equation of state. The solubilities *y* from this study were correlated with density ϱ according to

$$\ln y = a_1 \ln(\varrho/\text{kg m}^{-3}) + a_2 \qquad (1)$$

where a_1 and a_2 are two empirical constants that should be determined by fitting experimental data.

Table 4. Correlation of the Density Dependence of Solubility

pesticide	method	*T*/K	a_1	a_2	AARD (%)
endrine	1	313.1	5.16	−41.2	2.26
		333.1	4.87	−38.58	2.28
	2	313.1	5.18	−41.42	2.18
		333.1	5.18	−40.59	6.11
methoxychlor	1	313.1	5.63	−45.0	3.04
		333.1	5.45	−42.8	5.34
	2	313.1	5.18	−42.1	5.61
		333.1	5.18	−41.09	7.48
lindane	1	313.1	4.17	−34.39	1.22
		333.1	4.17	−33.53	1.56
	2	313.1	5.18	−41.17	7.31
		333.1	5.18	−40.11	19.8
DDT	1	313.1	5.24	−42.7	0.95
		323.1	5.02	−40.66	3.02
		333.1	5.15	−41.0	2.73
	2	313.1	5.18	−42.26	0.92
		323.1	5.18	−41.76	4.03
		333.1	5.18	−41.23	2.83

This formulation has been utilized previously (Stahl et al., 1978; Kumar and Johnston, 1988), although the density dependence of ln *y* can be linear or logarithmic in nature. Regression analysis confirmed that eq 1 is the most applicable to these results, and the regression coefficients are given in Table 4 (method 1). The constants a_1 and a_2 were allowed to vary for each compound and at each temperature. The results for DDT are included for comparison purposes. In all cases the correlation is good and the overall error from the regression has a similar magnitude to the expected experimental error (3%). This correlation was generalized when it was noticed that the solubilities for all of these compounds showed a similar density dependence. The correlation was modified so that a_1 became a constant for all of the solute + CO_2 systems at all pressures (including the DDT data from an earlier study). The results of this second regression analysis are also included in Table 4 (method 2). The average error from the second correlation is 6.2% compared to 2.3% with the first correlation, which is considered good because the total number of regressed parameters was reduced from 18 to 10 for the four systems. The temperature dependence of the intercept values a_2 for each compound exhibits similar trends.

Conclusion

The solubility of three chlorinated pesticides, endrin, methoxychlor, and lindane, have been measured in supercritical CO_2 at pressures between 100 and 220 bar and at temperatures of 313.1 and 333.1 K. The experimental error is estimated to be less than 3% on the basis of the average of three separate measurements for each reported solubility. The results exhibit trends that are typical of the solubility of nonvolatile organic molecules in supercritical CO_2. Correlating the solubility with the density of the CO_2 was successful with regression errors that matched the magnitude of the experimental errors.

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