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Phase Equilibria of Permethrin and Dicofol with Carbon Dioxide

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The solubilities of pesticides (permethrin and dicofol) in CO_2 were measured by a static-analytic method at pressures ranging from 10.0 MPa to 25.0 MPa and temperatures of 293.2 K, 303.2 K, and 313.2 K. Due to the nonconventional shape of some solubility isotherms, solid−liquid transitions of pesticides under pressure of CO_2 were determined using a modified capillary method. Since the solubilities depend on solvent density, the experimental binary solid−fluid equilibrium data were correlated as a function of solvent density by two different models.

Introduction

Supercritical fluid extraction (SFE) has been applied to remove toxic and nonvolatile pollutants from water, plant material, and other substrates.[1,2] A significant advantage of SFE over conventional handling processes is that there are no hazardous emissions. The pollutant molecules are often very complex in structure, and there are usually very few physical and chemical property data known about them. The solubility of pollutant species in the supercritical fluid is a very important factor in defining the performance of an extraction process.[3,4] Two pesticides of different chemical groups, which are often used in plant protection, were chosen for our study.

Permethrin has been chosen as a typical pyrethroid. Pyrethroids are synthetic forms of pyrethrins and tend to be more effective than natural pyrethrins while they are less toxic to mammals. Pyrethroids inhibit the nervous system of insects. Permethrin (CAS Registry No. 52645-53-1) is identified chemically as 3-phenoxybenzyl(1*RS*)-*cis*,*trans*-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropane carboxylate (Figure 1a).

Dicofol is an organochlorine acaricide used for control of crop-feeding mite pests. It has a moderate acute oral toxicity and a relatively high degree of acute dermal toxicity as being a nerve poison. Dicofol (CAS Registry No. 115-32-2) is identified chemically as 2,2,2-trichloro-1,1-bis(4-chlorophenyl) ethanol (Figure 1b).

In the present work, phase equilibria of permethrin + CO_2 and dicofol + CO_2 were examined. The solubility data were correlated by using two thermodynamic models relating the solubility of solute to the density of supercritical solvent. The detailed description of the model can be found in previous articles.[5−8]

Correlation Model: ln(w) versus ln(ρ_r). The expression relating the solubility of a solid solute in a supercritical fluid as a function of solvent density is given by[9]

$$w_i = \frac{P_i^{\text{sat}}}{\rho RT\Psi_i}\exp\frac{\nu_i^{\text{s}}(P - P_i^{\text{sat}})}{RT} \qquad (1)$$

where w_i is the equilibrium weight fraction of the solute in the supercritical phase (upper phase), P_i^{sat} is the saturated vapor pressure (MPa), ν_i^{s} is the molar volume of the solid solute (cm^3/mol), R is the universal gas constant (J/mol·K), P and T are the operating pressure (MPa) and temperature (K), and Ψ_i is the fugacity coefficient of the pure solute.

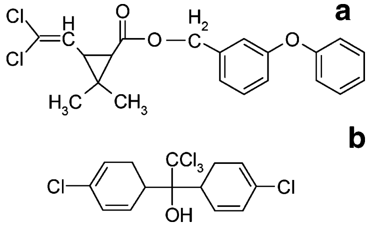

Figure 1. Chemical structure of (a) permethrin and (b) dicofol.

The final expression relating the solute solubility to solvent density is[6−8]

$$\ln(w_i) = \Theta \ln(\rho_r) + C_0 \qquad (2)$$

where C is a constant, Θ is the slope of the plot ln(w) against ln(ρ_r), and ρ_r is the reduced density of pure gas, determined as a quotient between density of gas at process conditions and critical density of pure gas ($\rho_r = \rho\rho_c^{-1}$).

Correlation Model by Chrastil. The model proposed by Chrastil[10] relates the solubility of a solute to the density of the supercritical solvent. It is based on the assumption that the molecule of a solute associates with the molecules of gas with formation of a solvato complex, which is in equilibrium with gas. The Chrastil equation (eq 3) can be written as

$$\ln(c) = k \ln(\rho) + \frac{a}{T} + b \qquad (3)$$

where c is the concentration of a solute in pure gas (g/m^3), ρ is the density of pure gas (kg/m^3), k is an association number, and a and b are constants.

Experimental Section

Materials. Permethrin (cis/trans 25/75, purity 93.6 %) was obtained from Belinka Belles (Ljubljana, Slovenia), and dicofol (purity 97.2 %, Cat. No. 36677) was obtained from Sigma (Seelze, Germany). Both were used without further purification. Carbon dioxide (purity 2.5) was supplied by

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Table 1. Physicochemical Properties of Permethrin and Dicofol

properties			permethrin	dicofol
molecular weight	M/g·mol^{-1}	FORMULA[a]	391.29	370.51
melting point	T_M/K	literature[b]	307.2−312.2	347.2−352.2
		measured	319.5	344.4
		measured in CO_2[c]		342.6
		measured in CO_2[d]		338.5
boiling point	T_b/K	JOBACK[a]	895.4	856.0
critical temperature	T_C/K	LYDERSEN[a]	1130.1	1102.1
critical pressure	P_C/MPa	LYDERSEN[a]	0.155	0.206
critical volume	V_C/cm^3·mol^{-1}	LYDERSEN[a]	1048	825
acentric factor	ω	DEFINITION[a]	0.9624	0.9751

[a] ASPEN software.[18] [b] Data from ref 17. [c] Measured with DSC (Thermoanalitical System Mettler TA 3000) under CO_2. [d] Measured with DSC under CO_2 after exposure to CO_2 in equilibria cell.

Messer (Ruše, Slovenia). *n*-Hexane and acetone were supplied by Merck (Darmstadt, Germany).

Determination of Solid−Liquid Transition under Pressure. The basic scheme of the experimental equipment used for determination of solid−liquid−gas (S−L−G) transition under pressure can be found in the literature.[11−15] The optical cell (35 mL) is designed for a pressure of 50.0 MPa and a temperature of 723.0 K. The two observation windows are made from sapphire glass and are fixed to the cell with screws. The cell is equipped with three additional openings for introducing and emptying the gas and one for a thermoelement. The thermoelement has been calibrated by pure substances with known melting points (*o*-nitrophenol $T_m = 318.2$ K, azobenzol $T_m = 341.2$ K, bisdiphenyl ketone $T_m = 368.2$ K, acetanilide $T_m = 388.2$ K).

The procedure for determining melting points of substances under pressure is based on the common method used at atmospheric pressure. The substance is filled in a glass capillary and put together with the thermoelement into the high-pressure cell. The gas is introduced, and pressure is measured by a high-pressure gauge (Digibar PE 200 Hottinger-Baldwin to ± 0.1 %). The cell is electrically thermostated by a heating jacket to within ± 0.5 K, and the temperature is measured by a thermocouple with an accuracy of ± 0.1 K.

The melting process (solid−liquid transition) of the substance in the capillary is observed visually by a camera. Temperature and pressure are registered at the beginning and at the end of the melting process. In screening experiments, it was checked whether observed melting temperature range depends on the mode of operation (pressure/temperature increase-upward strategy or pressure/temperature decrease-downward strategy). No hysteresis was found within experimental accuracy (± 0.2 K/± 0.05 MPa).

Determination of Solubility of Permethrin and Dicofol in CO_2. For the measurements of the solubility of substances in supercritical CO_2 a static-analytic method was used. The detailed description can be found in the literature.[6,7,13−16]

The equilibrium cell, which is a high-pressure autoclave (120 mL), was loaded with a sufficient amount (approximately 5 g) of the solid substance. A high-pressure pump was used to pump liquefied CO_2 into the autoclave. The solid and CO_2 phase were mixed at constant temperature and pressure with a magnetic stirrer until equilibrium was reached. The temperature in the high-pressure equilibrium cell was controlled by a thermocouple with an accuracy of ± 0.5 K, and the pressure was measured by a Digibar gauge, Hottinger Baldwin Messtechnik (accuracy ± 0.1 %). The time for reaching phase equilibrium and for sedimentation of solid particles was estimated to be 1 h for each, and a sample of substance−supercritical CO_2 solution was taken by means of a sampling valve into a solvent trap. The solvent trap used for permethrin samples was *n*-hexane, and acetone was used for dicofol samples, due to further analytical purposes. The solute solubilized in the solvent and the amount of CO_2 released (10 mL of gas at atmospheric conditions) was measured with a disposal of water in a graduated cylinder. The drop in the pressure observed while taking the sample was from (0.5 to 0.2) MPa, depending on pressure in the call. A temperature change was not detected. Since the quantity of the sample was sufficiently small as compared to the volume of the equilibrium cell, further experiments could have been performed after a particular time lapse needed to obtain equilibrium.

Analysis. The purity of permethrin-containing samples was determined by GC analysis (HP 5890A with flame ionization detector), and the purity of dicofol samples was determined with a UV spectrophotometer (Varian) at 210 nm. The estimated uncertainty of the concentration is approximately 0.03 wt %.

Results and Discussion

Physicochemical properties of the substances investigated are presented in Table 1. The melting points were obtained from literature[17] and were measured with a differential scanning calorimeter (DSC) in CO_2 atmosphere at normal pressure. The boiling point, critical temperature, pressure, and molar volume were estimated with the Lydersen group contribution method using ASPEN software.[18]

Phase Transitions of Permethrin and Dicofol under Pressure of CO_2. The S−L−G transitions of permethrin and dicofol under pressure of CO_2 are presented in Figure 2a,b. Each value was measured at least twice, and the relative standard deviation was 2.4 %. The S−L−G transitions of both substances were observed at pressure ranging from 0 MPa to 30.0 MPa and corresponding temperatures (Tables 2 and 3). From Figure 2a, it can be seen that the melting point of permethrin decreases with increasing pressure from 319.4 K at atmospheric conditions to 313.7 K at 12.0 MPa, after which it starts to increase again. At first, it increases slowly to 315.5 K at 17.5 MPa. With a further increase of pressure, a rapid increase of melting point to 319.2 K at 22.0 MPa is observed. In Figure 2b, it can be seen that the melting point of dicofol decreases from 344.6 K at atmospheric pressure to 320.2 K at 12.5 MPa, after which it remains approximately constant up to 30.0 MPa.

Solubility of Permethrin and Dicofol in CO_2. The experimental equilibrium solubilities of permethrin (Table 4) and dicofol (Table 5) were determined at temperatures of 293.2 K, 303.2 K, and 313.2 K and under pressures

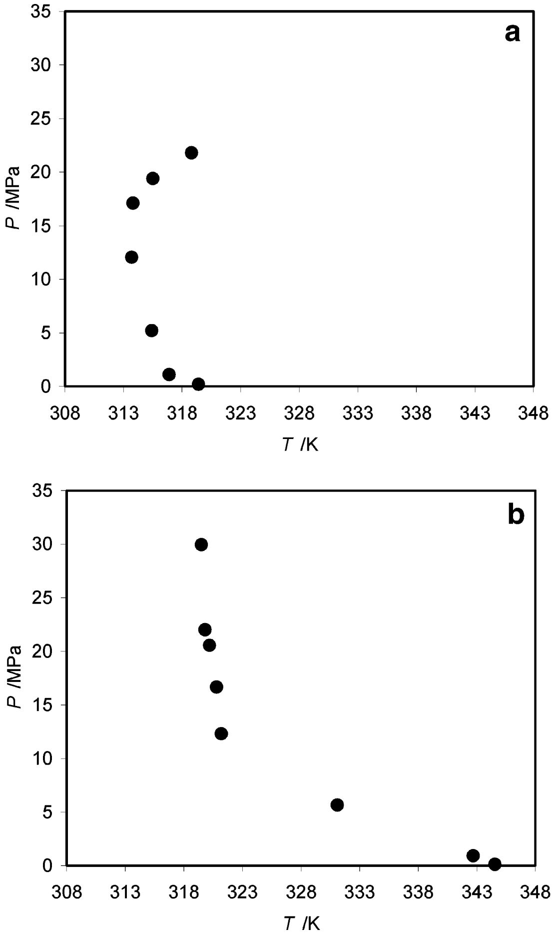

Figure 2. $P-T$ projection of the S−L-G curve for systems (a) permethrin + CO_2 and (b) dicofol + CO_2.

Table 2. Experimental S−L-G Transition Data of Permethrin

P/MPa	T/K	P/MPa	T/K
0.20	319.4	17.10	313.8
1.10	316.9	19.45	315.5
5.20	315.4	21.80	318.8
12.05	313.6		

Table 3. Experimental S−L-G Transition Data of Dicofol

P/MPa	T/K	P/MPa	T/K
1.0	344.6	16.65	320.8
9.0	342.7	20.55	320.2
5.65	331.1	22.05	319.8
12.35	321.2	29.95	319.5

ranging from 10.0 MPa to 25.0 MPa. Each data point represents the average of at least two measurements, and the relative standard deviation was 9.4 %.

The effect of pressure on the solute solubility in the compressed gas shows the usual trends, with the solubility increasing with increasing pressure for all three temperatures studied. As the system pressure is raised, the CO_2 density increases and the mean intermolecular distances of CO_2 molecules decreases, thereby increasing the specific interaction between the solute and solvent molecules. The next factor affecting the equilibrium solubility of a solid substance is the temperature of the system. The temperature influences the solute vapor pressure, the solvent density, and the intermolecular interactions in the fluid phase.

The weight fraction of permethrin rises with increasing pressure at 293.2 K from 1.27×10^{-2} (12.1 MPa) to 1.68×10^{-2} (20.4 MPa), at 303.2 K from 1.34×10^{-2} (12.0 MPa) to 1.75×10^{-2} (22.3 MPa), and at 313.2 K from 1.33×10^{-2} (11.7 MPa) to 2.05×10^{-2} (26.9 MPa). Temperatures above 313.2 K were not investigated in order to avoid the melting of permethrin.

Table 4. Experimental Equilibrium Solubility Data of Permethrin

T/K	P/MPa	$w^a \cdot 10^3$	T/K	P/MPa	$w^a \cdot 10^3$	T/K	P/MPa	$w^a \cdot 10^3$
293.2	12.05	12.7	303.2	12.00	13.4	313.2	11.65	13.3
	12.35	12.7		13.40	13.9		12.70	13.7
	13.45	12.9		14.40	14.3		13.05	15.0
	15.20	13.9		15.10	16.4		13.80	18.0
	16.05	15.3		16.05	17.1		14.55	19.6
	17.05	16.0		16.10	17.0		15.95	20.0
	19.50	16.7		16.70	17.1		20.80	19.8
	20.40	16.8		19.10	17.1		24.40	20.5
				22.25	17.5		26.90	21.3

[a] Weight fraction w/g·g^{-1}.

Table 5. Experimental Equilibrium Solubility Data of Dicofol

T/K	P/MPa	$w^a \cdot 10^3$	T/K	P/MPa	$w^a \cdot 10^3$	T/K	P/MPa	$w^a \cdot 10^3$
293.2	14.95	34.04	303.2	10.95	38.04	313.2	10.95	37.33
	21.45	37.55		15.20	39.38		15.35	39.42
	26.25	36.85		21.30	39.73		21.50	42.42

[a] Weight fraction w/g·g^{-1}.

For the binary system permethrin + CO_2, a slight inflection of the 313.2 K solubility isotherm in the pressure range from 16.0 MPa to 21.0 MPa could be observed. The unusual course of 313.2 K isotherm is probably a consequence of the fact that the isotherm lies very close to S−L−V line and a S−L phase transition of permethrin influences the solubility measurements. A similar unusual course of the solubility isotherm was already observed before for the capsaicin + CO_2[15] and vitamin D_2 + CO_2[14] systems. The solubility isotherm for the system permethrin + CO_2 lies practically on the three phase S−L−G line in the pressure range from 12 MPa ($\Delta T = T_{\text{melting point}} - T_{\text{isotherm}} = 0.5$ K) to 17.5 MPa ($\Delta T = 2.3$ K). With further increase of pressure, a rapid increase of melting point occurs (Figure 2a), so the 313.2 K solubility isotherm is shifted from the S−L−V line to the S−V region. In the same time the increase of solubility of permethrin in CO_2 can be observed.

The weight fraction of dicofol at 293.2 K slowly increases with pressure from 3.4×10^{-2} (14.9 MPa) to 3.8×10^{-2} (21.5 MPa) and then starts to decrease to 3.7×10^{-2} (26.2 MPa). At 303.2 K the solubility of dicofol steadily increases with increasing pressure, and the mole fraction ranges from 3.8×10^{-2} (10.9 MPa) to 4.0×10^{-2} (21.3 MPa). At 313.2 K it increases more rapidly with increasing pressure, and the weight fraction ranges from 3.7×10^{-2} (10.9 MPa) to 4.2×10^{-2} (21.5 MPa).

Solubility Correlation. According to the model, logarithm of solubility of the substance in supercritical CO_2 is a linear function of the logarithm of reduced solvent density. The plots $\ln(w)$ versus $\ln(\rho_r)$ are shown in Figures 3 and 4. Correlation constants determined from the plots and average absolute relative deviations (AARD) of calculated and experimental data are given in Table 6. The correlated lines have different slopes, which indicate that for each temperature different equations are necessary. No unique equation valid for all temperatures could have been obtained. The slope of the solubility isotherms decreases with higher temperature. In the case for permethrin the slope decreases from 4.6 at 293.2 K to 1.9 at 313.2 K; in case for dicofol the slope changes from a maximum value

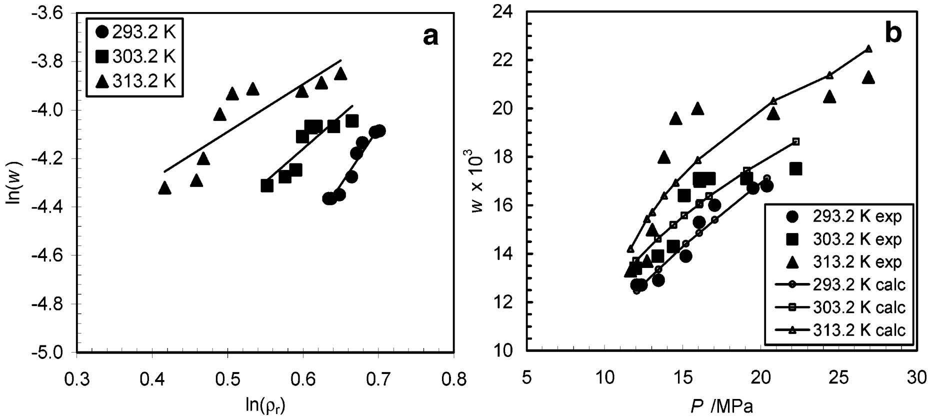

Figure 3. Solubility of permethrin in CO_2. (a) $\ln(w)$ vs $\ln(\rho_r)$ plot, (b) comparison of measured and calculated data with the $\ln(w)$ vs $\ln(\rho_r)$ correlation. ρ_r is reduced density of pure CO_2.

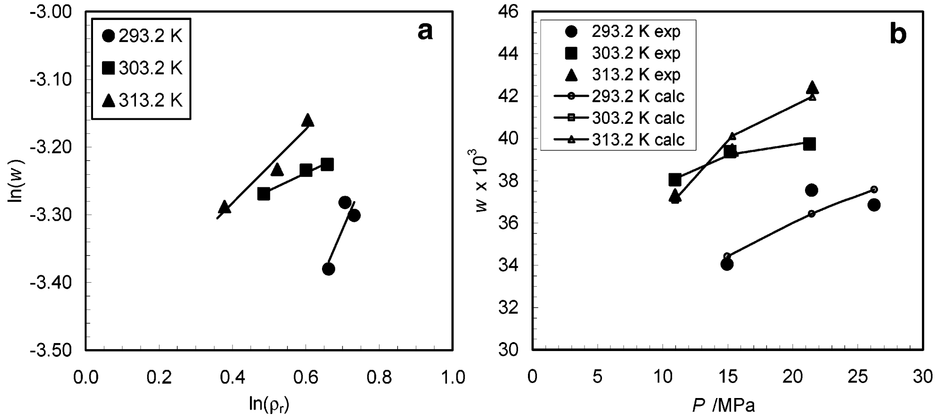

Figure 4. Solubility of dicofol in CO_2. (a) $\ln(w)$ vs $\ln(\rho_r)$ plot, (b) comparison of measured and calculated data with the $\ln(w)$ vs $\ln(\rho_r)$ correlation. ρ_r is reduced density of pure CO_2.

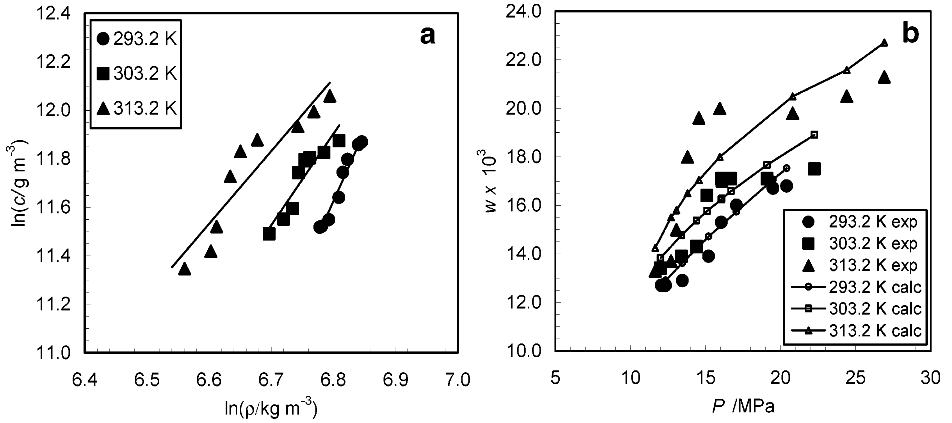

Figure 5. Solubility of permethrin in CO_2. (a) $\ln(c/g\cdot m^{-3})$ vs $\ln(\rho/kg\cdot m^{-3})$ plot, (b) comparison of measured and calculated data with the $\ln(c/g\cdot m^{-3})$ vs $\ln(\rho/kg\cdot m^{-3})$ correlation.

of 1.2 at 293.2 K to a minimum value of 0.2 at 303.2 K and then rises to 0.5 at 313.2 K. In the case of permethrin in CO_2, better linearity was obtained at 293.2 K where the AARD is 2.24 % and at 303.2 K and 313.2 K are 4.77 % and 7.73 %, respectively. In the case of dicofol, better linearity was obtained as in the case of permethrin. The AARD of calculated and experimental data at 293.2 K, 303.2 K, and 313.2 K were 2.02 %, 0.24 % and 1.12 %, respectively.

The Chrastil's model states that the logarithm of the solute concentration is a linear function of logarithm of solvent density. The association constant (k) is obtained from the slope of the line in a plot $\ln(c/g\cdot m^{-3})$ as a function of $\ln(\rho/kg\cdot m^{-3})$ at constant temperature (Figures 5 and 6).

Table 6. Constants and *AARD* Values of Correlation Model: $\ln(w^a)$ vs $\ln(\rho_r{}^b)$

	T/K	Q	C_0	AARD[c]/%
permetrin	293.2	4.6896	−7.3571	2.24
	303.2	2.7274	−5.7970	4.77
	313.2	1.9630	−5.0716	7.73
dicofol	293.2	1.2599	−4.2037	2.02
	303.2	0.2572	−3.3926	0.24
	313.2	0.5444	−3.5003	1.12

[a] Weight fraction $w/g\cdot g^{-1}$. [b] $\rho_r = \rho/kg\cdot m^{-3}\cdot\rho_c{}^{-1}/kg\cdot m^{-3}$. [c] AARD/% $= 1/N\sum_1^N(|w_{calc} - w_{exp}|)/w_{exp} \times 100$.

The results show that the slopes of the lines at three temperatures differ among each other. In case of solubility

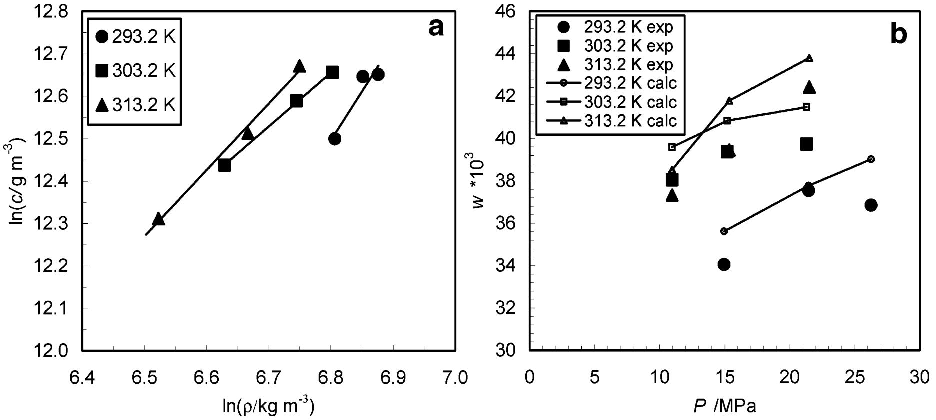

Figure 6. Solubility of dicofol in CO_2. (a) ln(c/g·m^{-3}) vs ln(ρ/kg·m^{-3}) plot, (b) comparison of measured and calculated data with the ln(c/g·m^{-3}) vs ln(ρ/kg·m^{-3}) correlation.

Table 7. Constants and AARD Values of the Correlation Model by Chrastil

	T/K	k	a	b	AARD^a/%
permethrin	293.2	5.7591	−1334.34	−22.9760	2.77
	303.2	3.7702		−9.3346	4.96
	313.2	2.9972		−3.9980	8.04
dicofol	293.2	2.3062	−651.35	−0.9641	3.70
	303.2	1.2675		6.1858	4.07
	313.2	1.5669		4.1650	4.12

^{a} AARD/% = $1/N \sum_1^N(|w_{\mathrm{calc}} - w_{\mathrm{exp}}|)/w_{\mathrm{exp}} \times 100$.

correlation for permethrin, the slope k decreases with increasing temperature from 5.7 at 293.2 K to 2.9 at 313.2 K. In the case for dicofol, the minimum value of k 0.2 was obtained at 303.2 K. In the following step, we have investigated the influence of approximating the slopes to be equal. The logarithm of concentration is a linear function of $1/T$ at constant density and has a slope given by constant a. The value of constant b has been calculated to minimize the deviation of the model from experimental data using a FORTRAN program. When approximating the slopes of lines to be equal, the AARD values are rather high, around 50 %. We concluded that the equation at each temperature should contain true values of the constants, and that there is no unique equation, which would be valid at all three temperatures, investigated. The consistency comparison is graphically shown in Figures 5 and 6.

From Figures 5 and 6, it is obvious that calculated values do in fact differ from the experimental values on average by 5.26 % for permethrin and 3.96 % for dicofol for the three temperatures under investigation (Table 7).

Conclusion

The solid−liquid-phase transitions and the equilibrium solubilities of two pesticides (permethrin and dicofol) in CO_2 were measured in order to obtain data for designing high-pressure extraction processes. The melting point of permethrin at atmospheric pressure was determined to be on average 319.7 K. Pressure of CO_2 influences the solid−liquid transition in the way that it decreases its melting point by almost 6 K at pressure of 12.0 MPa and 17.0 MPa. For dicofol the observed decrease in melting point is higher and is almost 24 K. This is an indication that the solubility of supercritical CO_2 in the melt of dicofol is relatively high, which leads us to some expectations about solubilities of both components in CO_2.

The experimental equilibrium solubilities of permethrin and dicofol in CO_2 were measured by a static-analytical method in the pressure range from 10.0 MPa to 25.0 MPa at temperatures of 293.2 K, 303.2 K, and 313.2 K. The solubility of dicofol in CO_2 is approximately 2 times higher than the solubility of permethrin in CO_2. Generally, the solubility of both pesticides in CO_2 is high enough to make the use of SFE with CO_2 feasible for removing these toxic substances from plants and other materials. Solubility data were correlated with two density-based models (ln(w) vs ln(ρ_r)) and Chrastil model. In both cases no unique equation valid for all temperatures investigated could be determined.

List of Symbols

a, b	numerical parameters of equation
c	concentration of a solute in a gas
C_0	empirical constant
k	compressibility
K	association number
v	molar volume
W	weight fraction of the solute in SCF phase
exp	experimental
calc	calculated

Greek Letters

Ψ	fugacity coefficient based on density of the phase
Θ	slope of the ln(w) versus ln(ρ_r)
ρ	density of the solvent
ρ_r	reduced density

Subscripts

i	component
r	reduced
M	melting
C	critical
b	boiling

Superscripts

sat	saturate
s	solid

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