

Characterization of Sorption of Endosulfan Isomers and Chlorpyrifos on Container Walls Using Mixed Solvent Systems

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The reliability of sorption data for organic contaminants with low water solubility has generated great concern because of the variability in the literature of the soil–water partition coefficient (K_{OC}) values for these compounds. In particular, sorption on container walls in aqueous systems when measuring the sorption coefficient, K_D (used to calculate K_{OC} values), for strongly hydrophobic compounds (SHOCs) is a potential source for discrepancies in the K_{OC} values. In this study, we eliminated sorption on container walls when measuring sorption of three halogenated compounds (α -endosulfan, β -endosulfan, and chlorpyrifos) using mixed solvents. Various mixtures of methanol and water were used. Sorption experiments were designed using polytetrafluoroethylene (Teflon)-lined centrifuge tubes and a high-performance liquid chromatography (HPLC) syringe. Solution sample analysis was performed using HPLC equipped with a UV diode array detector and C-18 column at a wavelength of 214 nm, with acetonitrile/water (80:20, v/v) as the mobile phase. The solvophobic model was used to calculate the percent recovery (% R_M) in water of the test compounds. Our results show that there is considerable sorption on container walls for the three chemicals at volume fractions of methanol ($f_c < 0.4$). The data show that, in aqueous systems, percent recoveries for α -endosulfan, β -endosulfan, and chlorpyrifos are 48, 45, and 61, respectively. Thus, to generate reliable sorption data for α -endosulfan, β -endosulfan, and chlorpyrifos and other SHOCs, experiments may be conducted using Teflon-lined centrifuge tubes and HPLC syringes at volume fractions of methanol ($f_c \geq 0.5$).

KEYWORDS: Solvophobic model; aqueous systems; percent recovery; Teflon-lined centrifuge tubes; HPLC syringes

INTRODUCTION

Sorption studies have been fundamental in the assessment of the fate of pesticides in soils and aquatic systems. As a result, considerable progress has been made in the understanding of sorption of pesticides from aqueous solutions by natural sorbents and aquifer materials. Studies have stretched from understanding sorption of hydrophobic organic compounds from aqueous solutions to sorption from mixed solvents (1–4). Correspondingly, several mathematical models have been proposed to describe sorption mainly based on the local equilibrium assumption. In these models, the sorption coefficient K_D of the organic pollutant and organic carbon sorption coefficient K_{OC} (obtained by normalizing K_D with soil organic carbon content) of contaminants are the basic parameters that have been used by environmental scientists and regulatory agencies worldwide in describing the environmental fate and behavior of pesticides (5, 6). However, the validity of sorption data for strongly hydrophobic organic chemicals (SHOCs) has generated great interest because of the variability in the soil–water partition coefficients (K_{OC}) values

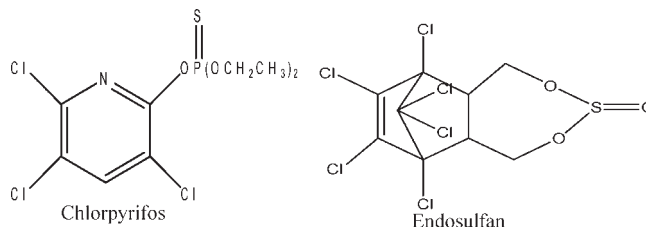
reported in the literature (7, 8). For chlorpyrifos [*o,o*-diethyl-*o*-(3,5,6-trichloro-2-pyridyl)phosphorothioate] and the two isomers (α and β) of endosulfan (6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzodioxathiopin-3-oxide), the reported K_{OC} values range from 3715 to 30900, from 2040 to 3980, and from 3550 to 19950, respectively (9–13). Similar variability of K_{OC} values for persistent organic pollutants (POPs) have been reported (7, 8).

Efforts have been made to evaluate the reliability of sorption data (8, 14). A great deal of earlier data for hydrophobic organic compounds involved single sorbate–single solvent systems (1, 15). However, because of the challenges in measuring the K_D value in aqueous systems, sorption models involving mixed solvent systems have since been developed. One of such theories is the solvophobic model, a theoretical approach based on the assumption of the predominance of solvophobic interactions formulated to quantitatively describe the sorption and transport of hydrophobic organic chemicals from aqueous and aqueous–organic-solvent mixtures (2–4, 14, 16–18). The application of such a model coupled with the use of centrifuge tubes lined with Teflon [polytetrafluoroethylene (PTFE)] during the experimental process have been widely assumed to eliminate uncertainties in the sorption data thus generated (8). Recent data for sorption of

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Table 1. Important Properties of Probe Chemicals

property	chemical		
	chlorpyrifos	α -endosulfan	β -endosulfan
aqueous solubility at 25 °C ($\mu\text{g mL}^{-1}$)	2 ^a	0.32 ^b	0.33 ^b
solubility in methanol at 25 °C ($\mu\text{g mL}^{-1}$)	116498 ^c	108000 ^d	108000 ^d
log K_{OC}	3.57–4.49 ^e	3.31 ^f , 3.60 ^g	3.55 ^f , 4.3 ^g
polar surface area PSA (\AA^2)	171.79 ^h	231.79 ^h	236.35 ^h
$\Delta\epsilon$ (erg \AA^{-2}) for PSA ⁱ	0.21×10^{-15}	0.21×10^{-15}	0.21×10^{-15}
k (erg K^{-1})	1.38×10^{-16}	1.38×10^{-16}	1.38×10^{-16}
T (K)	298	298	298
$\sigma_{\text{c-total}}^j$	11.80	13.56	13.56
$\sigma_{\text{c-PSA}}^j$	0.88	1.18	1.21
$\sigma_{\text{c-HSA}}^j$	10.92	12.38	12.36



^aFrom ref 9. ^bFrom ref 10. ^cFrom ref 19. ^dFrom ref 20. ^eFrom ref 21. ^fFrom ref 13. ^gFrom ref 11. ^hFrom ref 8. ⁱFrom ref 22. ^jCalculated in this study.

dieldrin, anthracene, and dichlorodiphenyltrichloroethane (DDT) on container walls of Teflon-lined centrifuge tubes and glass high-performance liquid chromatography (HPLC) vials developed using the solvophobic model have however proved that sorption on containers leads to errors that reduce the integrity of the analyte for strongly hydrophobic organic chemicals (8). Muwamba et al. (8) showed that, in a methanol–water system, there is considerable sorption of dieldrin, anthracene, and DDT on the Teflon-lined centrifuge tubes up to a fraction of methanol $f_c = 0.40$. This revelation is in contrast to the general assumption that most organic chemicals do not adsorb on Teflon-lined centrifuge tubes (made up of a polymer, PTFE). Thus, dependent upon the type of apparatus and equipment used during the analytical process of generating sorption data, SHOCs will be liable to sorption on these materials, which will greatly compromise the authenticity of the data generated. In this study, we present methanol fractions (f_c) for which sorption of chlorpyrifos and endosulfan isomers on surfaces of Teflon-lined centrifuge tubes and HPLC syringes is eliminated in a mixed solvent system of methanol and water.

MATERIALS AND METHODS

Analytical grades for chlorpyrifos, α -endosulfan, and β -endosulfan were obtained from Protocol Analytical, Metuchen, NJ, and Ultra Scientific, North Kingstown, RI. Chlorpyrifos is a broad spectrum, organophosphorus insecticide. On the other hand, endosulfan is a broad spectrum, non-systemic organochlorine insecticide. The technical endosulfan product (typically 96% active ingredient) is a mixture of two isomers, known as α (A or I) and β (B or II), in the ratio of 70–80% α to 30–20% β . Selected properties of the three pesticides are given in **Table 1**. Various mixtures of methanol and water were used as the binary solvents. HPLC-grade methanol was chosen to represent an organic co-solvent that is completely miscible with water. The 50 mL Teflon-lined centrifuge tubes used in the study were obtained from Fisher Scientific, Inc., Waltham, MA. An HPLC syringe and manual sample injection HPLC (Gilson model), equipped with a UV diode array detector and C-18 column at a wavelength of 214 nm, with acetonitrile/water (80:20, v/v) as the mobile phase, were used for analysis of the three probe pesticides.

Calculation of the Solubility and Sorption Coefficients of Solutes in Methanol–Water Mixtures. To estimate the solubility of α -endosulfan, β -endosulfan, and chlorpyrifos at various f_c , the solvophobic model (2, 3) was employed. This model has been applied to sorption of several organic compounds having moderate and intermediate hydrophobicity (3). The model is based on the relationship between the solubility of a

hydrophobic molecule in aqueous and mixed solvents and is expressed by the following equation (3, 22):

$$\ln X_m = \ln X_w + \sigma_c f_c \quad (1)$$

where X_m is the mole fraction solubility in mixed solvents, X_w is the mole fraction solubility in water, and f_c is the volume fraction of the co-solvent. The term σ_c reflects the solute–solvent interactions and is represented by the expression

$$\sigma_c = \frac{[\Delta\gamma_c \text{HSA} + \Delta\epsilon_c \text{PSA}]}{(kT)} \quad (2)$$

where $\Delta\gamma_c$ is the change in interfacial free energy at the organic co-solvent and water interfaces with hydrocarbonaceous surface area (HSA) of the organic molecule, $\Delta\epsilon_c$ is the change in interfacial free energy at the organic co-solvent and water interfaces with the polar surface area (PSA) of the organic molecule at ambient temperature T , and k is the Boltzmann constant. When $\Delta\epsilon_c \text{PSA} \ll \Delta\gamma_c \text{HSA}$, eq 2 reduces to eq 3 (see **Table 1**).

$$\sigma_c = \frac{[\Delta\gamma_c \text{HSA}]}{(kT)} \quad (3)$$

Equation 1 is based on the mole fraction solubility of the solute. The equation was modified to use the solubility of the solute in pure methanol and water that are available in the literature to calculate σ_c in (eq 3)

$$\ln \left[\frac{S_0}{S_w} \right] + 0.829 = \sigma_c \quad (4)$$

where S_0 ($\mu\text{g mL}^{-1}$) is the solubility in pure methanol and S_w ($\mu\text{g mL}^{-1}$) is the solubility in water; $\ln(32/18 \times 0.778) = 0.829$, where 32, 18, and 0.778 are the molecular masses of methanol and water and the density of methanol at 298 K, respectively.

Equation 5 based on the aqueous solubility of the solute was used to calculate the solubility of the solute in mixed solvents at any fraction co-solvent (f_c), in particular to make sure that the solubility at $f_c = 0.1$ of each compound was higher than the experimental initial concentration, C_0 (**Tables 2 and 3**)

$$S_M = \left[\left(\frac{S_w}{32} \right) (32 - 32f_c + 18f_c\rho) \right] \exp(\sigma_c f_c) \quad (5)$$

where S_M ($\mu\text{g mL}^{-1}$) is the solubility in mixed solvents at a given f_c and ρ (g mL^{-1}) is the density of methanol.

Calculation of Percent Recoveries (% R_M) at Various f_c . The relationship between sorption coefficients K_W and K_M in aqueous systems

Table 2. Sorption of α -Endosulfan, β -Endosulfan, and Chlorpyrifos on Surfaces of Teflon-Lined Centrifuge Tubes and an HPLC Syringe at Various Volume Fractions of Methanol (f_c)

methanol	α -endosulfan		β -endosulfan		chlorpyrifos	
f_c	$(C_e, \mu\text{g mL}^{-1})$	$(\% R_M)$	$(C_e, \mu\text{g mL}^{-1})$	$(\% R_M)$	$(C_e, \mu\text{g mL}^{-1})$	$(\% R_M)$
0.1	0.077	64.6	0.080	67.4	0.099	71.1
0.2	0.091	75.9	0.094	81.1	0.096	78.8
0.3	0.100	83.5	0.104	86.7	0.120	85.7
0.4	0.113	93.8	0.113	96.4	0.131	93.8
0.5	0.117	97.8	0.118	98.2	0.133	95.3
0.6	0.118	98.7	0.118	98.6	0.138	98.7
0.7	0.119	98.9	0.119	99.2	0.139	99.3
0.8	0.118	98.5	0.119	99.1	0.139	99.5
0.9	0.119	99.4	0.119	99.6	0.140	99.7

Table 3. Parameters of α -Endosulfan, β -Endosulfan, and Chlorpyrifos from Sorption on Surfaces of Teflon-Lined Centrifuge Tubes and an HPLC Syringe

parameters	chemical		
	chlorpyrifos	α -endosulfan	β -endosulfan
σ_c -total	11.80	13.56	13.56
σ_c -HSA	10.92	12.38	12.36
$\alpha_c \sigma_c$	4.45	5.12	5.74
α_c	0.41	0.41	0.46
$\% R_W$ (at $f_c = 0$)	61	48	45
negligible sorption (at f_c)	≥ 50	≥ 50	≥ 50
solubility at $f_c = 0.1$ ($\mu\text{g mL}^{-1}$)	6	1	1

and mixed solvents, respectively, is given by eq 6 (2, 3, 8), where α_c is an empirical constant. Other terms in eq 6 have been defined earlier.

$$\ln\left(\frac{K_M}{K_W}\right) = -\alpha_c \sigma_c f_c \quad (6)$$

The recovery of solute (R_M) from sorption on container walls is given in eq 7

$$R_M = \frac{C_e}{C_0} \quad (7)$$

where C_e is the equilibrium solution concentration ($\mu\text{g mL}^{-1}$) and C_0 is the initial concentration ($\mu\text{g mL}^{-1}$). Thus, if V is the volume of solution (mL) and A (cm^2) is the total surface area of the centrifuge tube and the HPLC syringe (that is used to inject the solution sample into the HPLC system) when the total surface area is covered by the solution, then the adsorbed equilibrium concentration S_e ($\mu\text{g cm}^{-2}$) is given as

$$S_e = \frac{V}{A} [C_0 - C_e] \quad (8)$$

At equilibrium, the linear Freundlich isotherm is such that

$$S_e = K_M C_e \quad (9)$$

where K_M (mL cm^{-2}) is the sorption coefficient in mixed solvents. Substituting eqs 7 and 8 into eq 9 gives eq 10 in terms of K_M and K_W

$$K_M = \frac{V}{A} \left[\frac{1}{R_M} - 1 \right] \quad (10a)$$

$$K_W = \frac{V}{A} \left[\frac{1}{R_W} - 1 \right] \quad (10b)$$

where K_W (mL cm^{-2}) is the sorption coefficient in water and R_W is the fraction of the solute recovered in water ($f_c = 0$).

Substituting eqs 10a and 10b into eq 6 produces eq 11.

$$\left[\frac{1}{R_M} - 1 \right] = \left[\frac{1}{R_W} - 1 \right] \exp(-\alpha_c \sigma_c f_c) \quad (11)$$

Log transformation of eq 11 gives eq 12

$$\ln \left[\frac{1}{R_M} - 1 \right] = \ln \left[\frac{1}{R_W} - 1 \right] - (\alpha_c \sigma_c f_c) \quad (12)$$

Therefore, a plot of $\ln[(1/R_M) - 1]$ against f_c is linear with an intercept equal to $\ln[(1/R_W) - 1]$. The intercept is used to calculate the solute recovery in water (R_W) at $f_c = 0$.

Percent recoveries ($\% R_M$) at various f_c values were then obtained from eq 13 based on eq 12.

$$\% R_M = \left[\frac{1}{1 + \left(\frac{1}{R_W} - 1 \right) \exp(-\alpha_c \sigma_c f_c)} \right] \times 100 \quad (13)$$

Equation 13 is the model that was used to describe percent recoveries as a function of f_c .

Sorption of Chlorpyrifos, α -Endosulfan, and β -Endosulfan on Container Wall Surfaces of Teflon-Lined Centrifuge Tubes and a HPLC Syringe. A volume of 1 mL of α -endosulfan or β -endosulfan standard concentration ($6 \mu\text{g mL}^{-1}$ in methanol) and 1 mL of chlorpyrifos standard concentration ($7 \mu\text{g mL}^{-1}$ in methanol), respectively, were pipetted into various 50 mL centrifuge tubes. Various volumes of methanol (without the chemical) and 0.01 M CaCl_2 solution were added to the centrifuge tubes to make a total volume of 50 mL and different volume fractions of methanol (f_c from 0 to 0.9). This gave solutions of initial concentrations (C_0) of $0.12 \mu\text{g mL}^{-1}$ for α - and β -endosulfan and $0.14 \mu\text{g mL}^{-1}$ for chlorpyrifos in the corresponding tubes.

The samples were shaken for 3 h using a Glass-Col at 30% revolution and then left to equilibrate at room temperature (for 24 h), after which the suspensions were analyzed with HPLC (23, 24). The ratio of the solution equilibrium concentration and the initial concentration gave the percent recovery ($\% R_M$) = $(C_e/C_0) \times 100$ from the adsorption on the walls of the containers (centrifuge tube + syringe) at that fraction of co-solvent (f_c). The adsorbed solute by some of the centrifuge tubes and syringe was extracted with 100% methanol. After analysis of the extracts, mass balance confirmed that the amount of solute not recovered was adsorbed on container walls.

RESULTS AND DISCUSSION

Equilibrium solution concentrations (C_e) and percent recovery ($\% R_M$) for α -endosulfan, β -endosulfan, and chlorpyrifos from sorption on Teflon-lined centrifuge tubes in combination with a HPLC syringe at various volume fractions of methanol (f_c) are presented in **Table 2**. The data indicate that, in 10% methanol ($f_c = 0.1$), 65, 67, and 71% of α -endosulfan, β -endosulfan, and chlorpyrifos, respectively, remained in the mixture of methanol and water.

Although working in mixed solvents has always been believed to eliminate sorption on container walls, results in **Table 2** indicate that, even at 40% methanol in the mixture, there was pesticide sorption on container walls. Muwamba et al. (8) found that there was negligible sorption of DDT and dieldrin by Teflon-lined centrifuge tubes in a mixture of 40% methanol in water. Because the three probe compounds used in this study are much less hydrophobic than DDT that has aqueous solubility of $0.003 \mu\text{g mL}^{-1}$ (8), this suggests that, in addition to sorption on walls of the Teflon-lined centrifuge tubes that were used in sorption experiments, the chemicals were exposed to other surfaces onto which they adsorbed. In the case of HPLC analysis, the technique used in this study, the possible steps where the chemicals would adsorb before analysis include preparation of standard solutions, transfer of solutions to centrifuge tubes, the centrifuge tubes themselves (8), and HPLC syringe if one is using a manual injection, as was the case in this study. In this study, standard solutions for all three test pesticides were prepared in Teflon-lined centrifuge tubes using pure methanol to eliminate

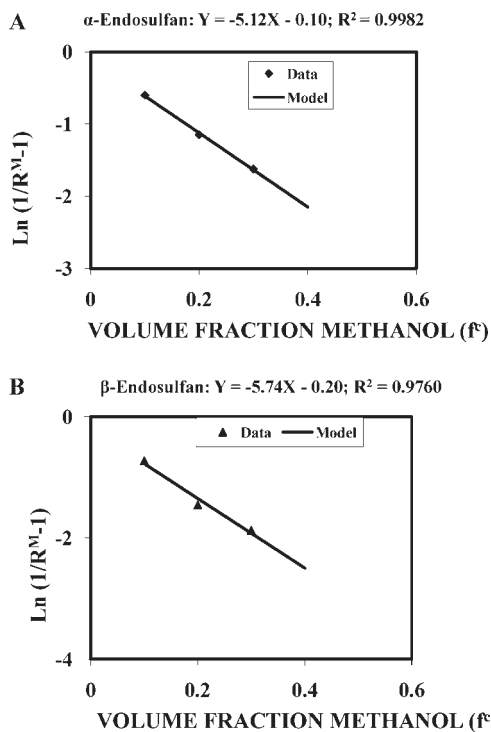


Figure 1. Plot of $\ln(1/R_M - 1)$ against f_c for (A) α -endosulfan and (B) β -endosulfan.

sorption on the container walls. However, an account was not separately made for the sorption of the three chemicals by surfaces of the HPLC syringe, which is composed of a stainless-steel plunger, a graduated glass tube, and a stainless-steel needle. Thus, sorption on container walls should include the centrifuge tubes and the syringe surfaces.

Analysis of the data in Table 2 using the solvophobic model given in eq 12 show that a log linear relationship exists between $\ln[(1/R_M) - 1]$ and f_c (Figures 1 and 2) in the range of f_c from 0.1 to 0.3. Similar relationships were observed by Muwamba et al. (8) for the sorption of DDT, dieldrin, and anthracene on surfaces of Teflon-lined centrifuge tubes. The slopes of the lines in Figures 1 and 2 are the estimation of the values of parameters $\alpha_c \sigma_c$. The values are very close for the two isomers of endosulfan, but chlorpyrifos has a much smaller value. Therefore, the parameter α_c is dependent upon the interactions between the sorbate and the sorbent, because σ_c obtained from mixtures of methanol and water is independent of the sorbent based on eq 2 (2, 3, 8).

Using literature solubility data of the three probe compounds in pure methanol and water (Table 1), the parameter σ_c -total was calculated as 11.80, 13.56 and 13.56 for chlorpyrifos, α -endosulfan, and β -endosulfan, respectively (Table 3). The parameter σ_c -total was then used to calculate the values of σ_c -HSA for chlorpyrifos, α -endosulfan, and β -endosulfan, which were 10.92, 12.38, and 12.36, respectively (Table 3). Data in Tables 1 and 3 indicate that the assumption ($\Delta \epsilon_c \text{PSA} \ll \Delta \gamma_c \text{HSA}$) for the three test compounds is valid. Therefore, we assumed that hydrophobic interactions were predominant in our system and that eq 12 describes the sorption process of test compounds by container walls in methanol–water mixtures. Because such values of σ_c -HSA (Table 3) were used to calculate the empirical coefficient α_c , all three α_c values are less than 1 compared to values obtained by Muwamba et al. (8) for DDT, dieldrin, and anthracene for sorption on Teflon-lined centrifuge tubes that were very close to 1. This implies that, in our system, there was a combined effect of interactions of test compounds with Teflon plus HPLC syringe

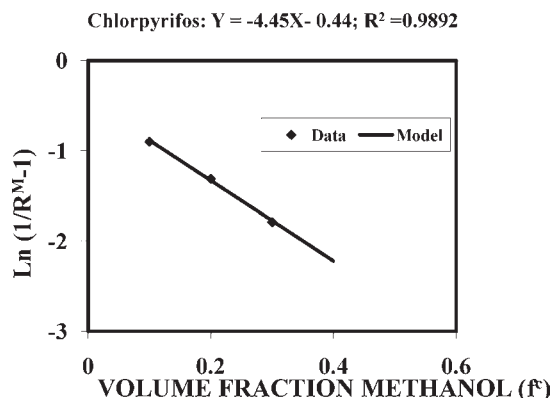


Figure 2. Plot of $\ln(1/R_M - 1)$ against f_c for chlorpyrifos.

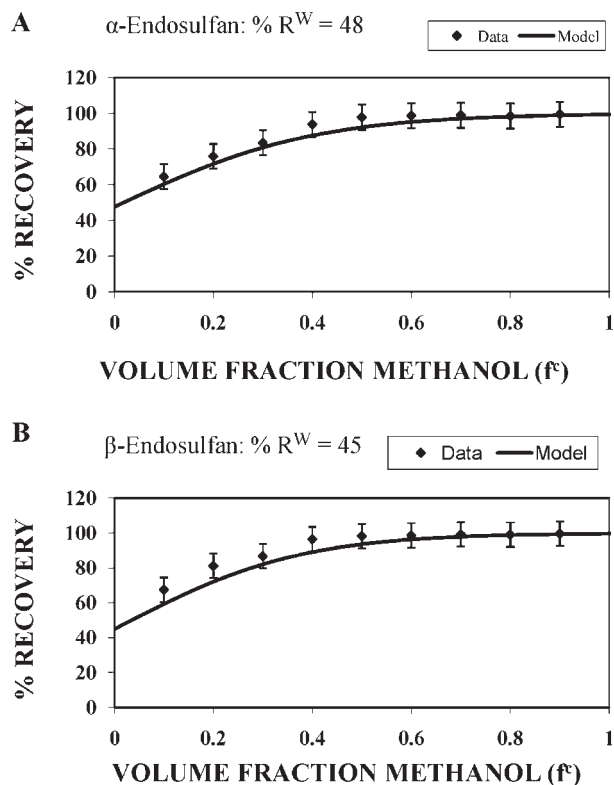


Figure 3. Plot of $\% R_M$ against f_c for (A) α -endosulfan and (B) β -endosulfan.

surfaces. The α_c values of much less than 1 (Table 3) are attributed to resistance of compounds on surfaces of container walls against desorption by the co-solvent–water mixture and decreased affinity of the compounds to the sorbent surfaces (4, 25).

The data in Figures 3 and 4 were well-described by the model (eq 13). Note that the model parameters were generated using data at f_c between 0.1 and 0.3. In this range of f_c , the model was linear and the amount of solute adsorbed was more than 15% (Table 2). However, the model simulations covered f_c in the range of 0–1. The data indicate that, at 50% methanol and above ($f_c \geq 0.5$), there was negligible sorption of the probe compounds on the surfaces of Teflon-lined centrifuge tubes and the HPLC syringe, suggesting that that sorption experiments conducted in aqueous solutions or at volume fractions of methanol ($f_c < 0.5$) may lead to variability in sorption data of the three chemicals if sorption on container walls is not taken into account. From the model simulations, it was estimated that the percent recovery from sorption of α -endosulfan, β -endosulfan, and chlorpyrifos in aqueous systems would be 48, 45, and 61,

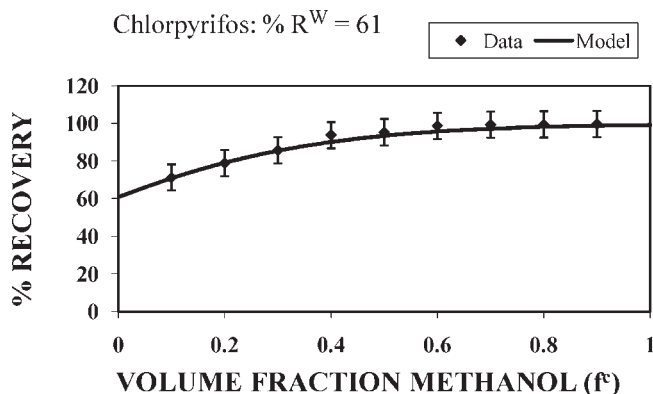


Figure 4. Plot of % R_M against f_c for chlorpyrifos.

respectively (Figures 3 and 4 and Table 3). This implies that sorption experiments conducted in aqueous solutions or at volume fractions of methanol ($f_c < 0.5$) may lead to questionable sorption data (K_{OC} values) for the three chemicals studied and other strongly hydrophobic organic chemicals. We anticipate similar errors because of sorption on container walls to occur when aqueous solutions of POPs and other SHOCs are collected or analyzed using containers made of Teflon, plastic, or glass. This may explain why there are wide variations in the K_{OC} values reported in the literature when sorption on container walls is not taken into account. Such data are 3715–30 903 for chlorpyrifos, 2041–3981 for α -endosulfan, and 3548–19 953 for β -endosulfan (9–13, 23). Therefore, to eliminate the effect of sorption on container walls, the sorption data for chlorpyrifos, α -endosulfan, and β -endosulfan generated using Teflon-lined centrifuge tubes and an HPLC syringe can be determined in methanol–water systems at volume fractions of methanol (f_c) of more than 0.5, as long the linear model (eq 6) is valid.

ABBREVIATIONS USED

C_e , equilibrium solution concentration; C_o , initial solution concentration; f_c , volume fraction of co-solvent (subscript c denotes co-solvent); HSA, hydrocarbonaceous surface area of a molecule; k , Boltzmann constant; K_D , soil–water partition coefficient; K_M , sorption coefficient in mixed solvents; K_{OC} , soil–water partition coefficient normalized with soil organic carbon content; K_{OW} , octanol–water partition coefficient; K_W , sorption coefficient in water; OC, organic carbon content in the soil; PTFE, polytetrafluoroethylene (Teflon); PSA, polar surface area of a molecule; R_M , recovery of solute in mixed solvents; R_W , recovery of a solute in water; % R_M , percent recovery of a solute in mixed solvents; S_e , equilibrium adsorbed concentration of a solute; SHOC, strongly hydrophobic organic chemical; S_o , solubility of a solute in pure organic solvent; S_M , solubility of a solute in mixed solvents; S_W , solubility of a solute in water; T , ambient temperature; X_m , mole fraction solubility of a solute in mixed solvents; X_w , mole fraction solubility of a solute in water; α_c , empirical constant in mixed solvents; $\Delta\gamma_c$, change in interfacial free energy at the interface of co-solvent, water, and HSA; $\Delta\epsilon_c$, change in interfacial free energy at the interface of co-solvent, water, and PSA; ρ , density of co-solvent; σ_c -HSA, co-solvency power as a result of the HSA of a molecule; σ_c -PSA, co-solvency power as a result of the PSA of a molecule; σ_c -total, total co-solvency power as a result of both HSA and PSA of a molecule.

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