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An assessment of solubility profiles of structurally similar hazardous pesticide in water + methanol mixture and co-solvent effect on partition coefficient

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Abstract

This paper reports solubility and partition coefficient data for the structurally similar pesticides, fenvalerate and cypermethrin, measured by UV spectrophotometry in binary mixtures of methanol and water at different temperatures. The solubility of both pesticides is much higher in methanol than in water at all temperatures. Partition coefficients were also measured between water + heptanol immiscible mixtures at 298.15 K, and these data show a decrease with increasing composition of methanol in water. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Solubility; Fenvalerate; Cypermethrin; Partition coefficient; Pesticide

1. Introduction

The extensive use of pesticides in modern agricultural development in order to increase the production of food grains has created concern about their hazardous effects in the environment, thereby creating a threat to human and animal hygiene [1–3]. Crops can be protected by pesticides, but their heavy usage can result in environmental pollution; most pesticides when used without caution can be extremely poisonous to the plants. Illness due to pesticide exposure has been a serious and pandemic problem with farmers. Also, pesticide contamination of surface and ground water can be hazardous to drinking water sources. In order to understand the fate of toxic pesticides and to propose safe methods for their use, it is important to assess the solubility and partition characteristics of these pesticides in aqueous organic mixtures even before they are actually used in the field.

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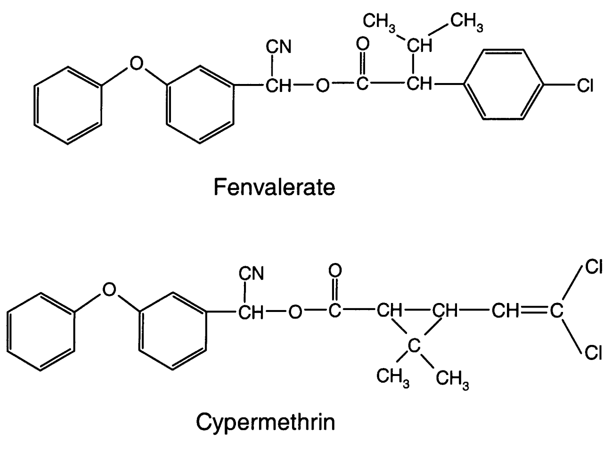
In this study, we have selected fenvalerate [(*RS*)-α-cyano-3-phenoxybenzyl(*RS*)-2-(4-chlorophenyl)-3-methylbutyrate] and cypermethrin [(*RS*)-α-cyano-3-phenoxybenzyl-(1, *RS*)-*cis*–*trans*-3-(2,2-dichlorovinyl)-2,2-dimethyl cyclopropane carboxylate] as model pesticides to evaluate their solubility profiles in polar to non-polar solvent mixtures. These pesticides are well known in agriculture and have a structural similarity, yet exhibit different activity. The purpose of studying solubility profiles was to create a database that will be useful in the selection of appropriate solvent mixtures for the effective extraction of pesticides from various samples to determine their residual toxicity [4]. Additionally, such data would be important in developing controlled release formulations of similar pesticides to obtain environmentally friendly products with reduced toxicity [5].

2. Materials and methods

A 92 mass% pure grade fenvalerate and 94.4 mass% pure grade cypermethrin (see Scheme 1) were provided as gift samples from Rallis India Limited Industries, Bangalore, India. These were further purified by dissolving in AR grade acetone and precipitated in double distilled water. Methanol (HPLC grade) and heptanol (AR grade) samples were purchased from s.d. Fine Chemicals, Mumbai, India. Double distilled water was used; its purity was checked by comparing its conductivity with the literature, which agreed well.

Methanol + water mixtures were prepared by mixing an exactly weighed amount of methanol and water by using a single pan Mettler electronic balance (Model AE 240, Switzerland) with an accuracy of ±0.01 mg. A total of 10 compositions of solvent mixtures in 100 ml volumetric flasks were prepared to obtain the solubility of fenvalerate and cypermethrin. The same experimental method was adopted for both pesticides. In each of these flasks, an excess amount of fenvalerate/cypermethrin was added to ensure maximum solubility and the mixtures were shaken thoroughly for 15 min, then kept in a water bath (Grants, Model Y14, UK) previously maintained at 298.15, 303.15, and 308.15 K within an



Scheme 1. Structure of the pesticides.

accuracy of ±0.1 K at the desired temperature. The flasks were allowed to stand for 12 h to attain equilibrium as well as to separate the undissolved droplets of cypermethrin/fenvalerate completely. A 10 ml aliquot of the mixture was taken out from the aqueous layer, diluted with the same system and then the absorbance was measured at the λ_{max} value of 277 nm for both pesticides by using a UV spectrophotometer (Anthelie, Secomam, France).

The partition coefficient of cypermethrin/fenvalerate in water + heptanol immiscible mixtures was measured by adding 150 mg of fenvalerate or cypermethrin in 100 ml of volumetric flask containing 50 ml each of heptanol + distilled water previously maintained at a temperature of 298.15 K. To study the effect of co-solvent (methanol) on partition of fenvalerate/cypermethrin, various amounts of methanol were added to 50 ml of heptanol taken in a 100 ml volumetric flask; then its volume was adjusted to 100 ml by adding distilled water. In order to calculate the effect of methanol on the partition coefficient of fenvalerate, various mass% of methanol were added. Since methanol is soluble in heptanol and water, the distribution of methanol itself in water + heptanol mixtures was studied by measuring the refractive index (Abbe's refractometer, model Attago 3T, Japan) of pure heptanol, pure methanol and their mixtures. After complete distribution of methanol in the water + heptanol system the mass% of methanol in water was calculated using the distribution constant value of methanol. To this solvent mixture, about 150 mg of fenvalerate or cypermethrin was added and the mixture was shaken thoroughly for 30 min and allowed to stand for 12 h to attain equilibrium at a constant temperature of 298.15 K. To estimate the amount of fenvalerate/cypermethrin present in each phase, a 5 ml aliquot of organic phase was taken out, diluted wherever necessary and the absorbance measured at 277 nm for both pesticides. The amount of fenvalerate/cypermethrin in the aqueous phase was calculated by mass balance and also confirmed by taking a 5 ml aliquot of the aqueous phase and diluting it with the same solvent mixture (i.e. water + methanol) and its absorbance was measured at 277 nm for both pesticides.

3. Results and discussions

The solubilities of fenvalerate and cypermethrin in water + methanol mixtures are presented in Tables 1 and 2. The solubility of fenvalerate in methanol is higher than that in water at all temperatures (see Fig. 1). The addition of methanol to water increases the solubility of fenvalerate by about 10-fold after the addition of 40 mass% of methanol. However, a 100-fold increase in solubility is observed when 60 mass% of methanol is added. Fenvalerate being hydrophobic, has poor water solubility and by increasing the amount of methanol in water the hydrophobicity increases and hence, the solubility for fenvalerate. The temperature dependence of solubility for fenvalerate is less in water when compared to pure methanol. However, this dependency increases with an increase in mass% of methanol.

Similar observations may be made with cypermethrin. The presence of two chloride groups in the structure of cypermethrin makes it more soluble in water than fenvalerate by about 25-fold, which is due to hydrogen bonding with water molecules. The solubility data for cypermethrin in pure water and water + methanol mixtures are presented in Table 2. The addition of 60 mass% of methanol to water increases the solubility of cypermethrin by about 20-fold (see Fig. 2). A further 600-fold increase is observed for 90 mass% of methanol in

Table 1
Solubility of fenvalerate in methanol + water mixtures at different temperatures

Mass% of methanol	Solubility of fenvalerate (μg/ml)		
	298.15 K	303.15 K	308.15 K
0	2.6 ± 0.2	5.0 ± 0.2	12.5 ± 0.3
9.9	3.1 ± 0.2	7.8 ± 0.8	13.1 ± 0.8
19.0	4.5 ± 0.3	11 ± 0.8	16.9 ± 7
30.4	6.7 ± 0.5	13.2 ± 0.8	21.5 ± 8
40.6	25.8 ± 0.3	42 ± 1.5	86.4 ± 6
48.0	65.9 ± 0.1	83.6 ± 2	176.7 ± 40
59.8	245 ± 4.0	1010 ± 53	2196 ± 11.5
69.4	857 ± 19	3785 ± 45	8795 ± 508
79.4	3905 ± 33	18833 ± 91	28365 ± 2451
100	199808 ± 22255	216923 ± 16790	246418 ± 15489

water. It may be noted that by increasing the amount of methanol in water the hydrophilic nature of water decreased and hence, the solubility of cypermethrin increased. Solubility of both the pesticides in the selected binary mixtures is considerable even for every 5 K increase in temperature; solubility increases by about 2-fold even in this short interval of temperature. However, cypermethrin is freely soluble in methanol.

The partition coefficients of fenvalerate and cypermethrin and the effect of methanol on the water + heptanol partition coefficient was studied at 298.15 K. These results are given in Table 3. Since fenvalerate and cypermethrin are highly soluble in heptanol; the partition coefficient is also high. Earlier, *Garnas and Schimmel* [6] reported the partition coefficient data for fenvelerate in water + octanol mixture to be $\log P = 6.5$. In the present work, partition coefficient data was obtained below the saturation concentration of fenvalerate and cypermethrin in the aqueous phase. Our calculated value for the partition coefficient of fenvalerate in water + heptanol mixture is 23.68 ($\log P = 1.4$) at 298.15 K. The measured value of the partition coefficient of cypermethrin in water + heptanol mixture is 260.0

Table 2
Solubility of cypermethrin in methanol + water mixtures at different temperatures

Mass% of methanol	Solubility of cypermethrin (μg/ml)		
	298.15 K	303.15 K	308.15 K
0	76 ± 0.3	224 ± 1	433 ± 2
10.7	179 ± 0.4	409 ± 2	504 ± 4
20.2	220 ± 0.6	456 ± 2	613 ± 7
29.3	262 ± 0.5	576 ± 2.8	674 ± 8
35.2	317 ± 0.6	617 ± 3.0	849 ± 9
48.2	655 ± 0.8	1457 ± 6	2041 ± 35
61.0	1750 ± 6.3	3429 ± 48	5301 ± 62
73.8	6639 ± 29	12121 ± 65	20232 ± 618
80.2	20673 ± 28	40961 ± 91	63268 ± 245
90.2	43269 ± 150	80267 ± 286	111239 ± 545

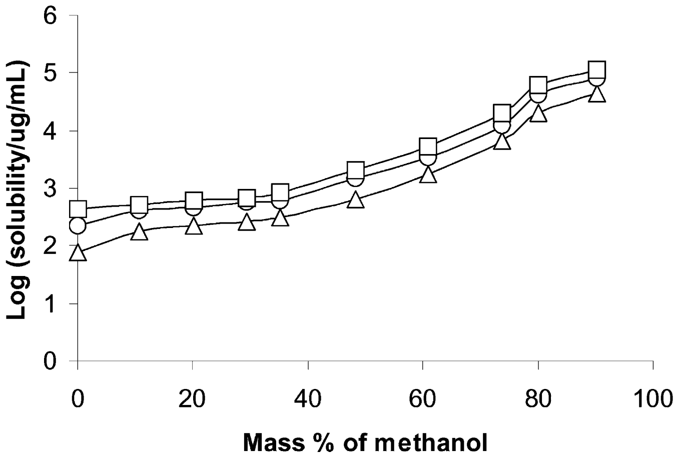


Fig. 1. Solubility of fenvalerate in methanol + water mixture at (△) 298.15 K, (○) 303.15 K and (□) 308.15 K.

(log $P = 2.417$) at 298.15 K. The results of partition coefficient for fenvalerate and cypermethrin obtained in water + heptanol mixtures along with the effect of methanol on partition coefficients measured at 298.15 K are given in Table 3.

In order to calculate the effect of methanol on the partition coefficient of fenvalerate, various mass% amounts of methanol were added to water + heptanol mixture and these results are included in Table 3. Since methanol is soluble in heptanol and water, the distribution of methanol itself in water + heptanol mixture was studied by measuring the refractive index of pure heptanol, pure methanol and their mixtures. After complete distribution of methanol in the water + heptanol mixture, the mass% of methanol in water was calculated using the

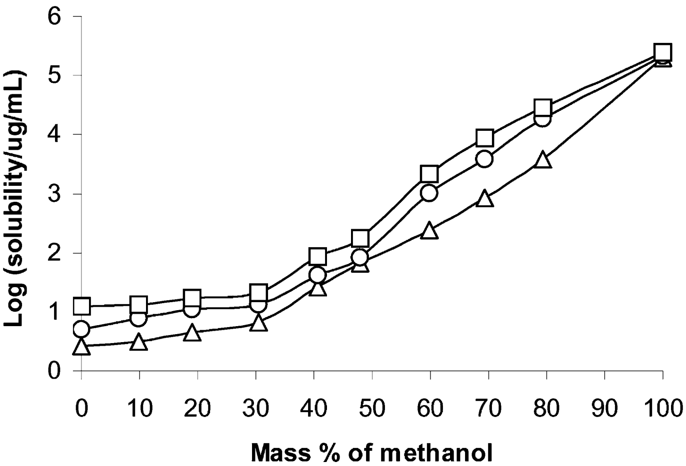


Fig. 2. Solubility of cypermethrin in methanol + water mixture at (△) 298.15 K, (○) 303.15 K and (□) 308.15 K.

Table 3
Distribution of methanol between heptanol and water, and effect of co-solvent (methanol) on partition coefficient of (A) fenvalerate and (B) cypermethrin at 298.15 K

Mass% of methanol in water after distribution	Amount of pesticide added (mg)	Pesticide (mg)		Partition coefficient
		Organic phase	Aqueous phase	
(A) Fenvalerate				
0	185.8	178.27	7.53	23.68
10.2	135.3	127.70	7.60	16.80
15.9	116.2	109.12	7.09	15.39
22.3	198.3	185.23	13.07	14.17
29.3	128.4	119.73	8.62	13.89
(B) Cypermethrin				
	193.05	192.31	0.74	260.0
	240.76	239.67	1.09	220.0
	240.12	238.52	1.60	150.0
	222.97	219.68	3.29	66.8
	175.43	169.29	6.14	27.6
Mass of methanol (g)	Mass of methanol in heptanol (g)	Mass of methanol in water (g)	Distribution constant	
7.81	3.20	4.60	0.695	
11.85	4.86	6.99	0.695	
15.80	6.48	9.32	0.695	
19.75	8.10	11.65	0.695	

distribution constant value of methanol. However, addition of methanol as a co-solvent to water decreases the partition coefficient of both fenvalerate and cypermethrin (see Figs. 3 and 4). This is due to the fact that addition of methanol in the water phase increases the solubility of pesticide in water thereby decreasing the partition coefficient of fenvalerate and cypermethrin.

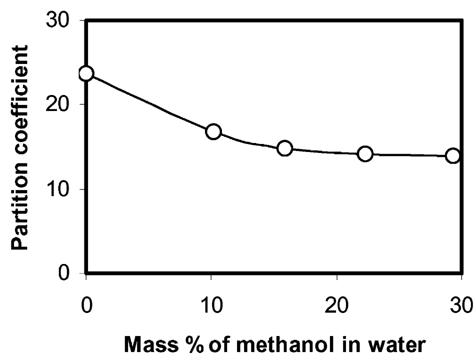


Fig. 3. Effect of methanol on partition coefficient of fenvalerate at 298.15 K.

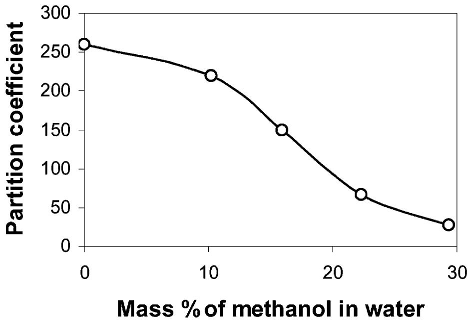


Fig. 4. Effect of methanol on partition coefficient of cypermethrin at 298.15 K.

4. Conclusions

The present paper is a continuation of our ongoing program of research on the development of environmentally friendly pesticide-loaded polymeric matrices for the release of hazardous pesticides in the soil. The toxicity of these two broad-spectrum pesticides, fenvalerate and cypermethrin, has been of some concern to farmers. However, by adopting suitable methods, it is possible to encapsulate such toxic pesticides using a polymeric matrix thereby reducing their toxicity levels. Such products can provide a safe usage in field applications.

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