Comparative Study of Release Kinetics of Pheromone from Polymer Dispensers

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ABSTRACT: Polymer membranes loaded with agrochemicals are used as controlled release monolithic dispensers in pest control. Plasticized poly(vinyl chloride) dispensers loaded with a fixed concentration of gossyplure pheromone were prepared by a solution-casting method. A solvent trap system was designed and fabricated to collect the gossyplure released from the dispenser at desired intervals of time. The release of pheromone was estimated quantitatively by using high-performance liquid chromatography. The rate of release is found to be slightly higher in the first 12 h and then it became steady, obeying Fick's law of diffusion. The diffusion coefficient of the pheromone is observed to be directly proportional to the concentration of the plasticizer in the dispenser. Simultaneously, the rate of release of pheromone from the dispenser was also determined by a gravimetric desorption method. The diffusion coefficient data obtained from the gravimetric desorption method was found to be fairly comparable to that obtained from high-performance liquid chromatographic estimation. The results indicate the authenticity and reliability of the gravimetric desorption method. The dispensers were found to release gossyplure at reasonably controlled rates even after 30 days.
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Key words: polymer membranes; gossyplure pheromone; diffusion coefficient; gravimetric desorption; release kinetics; poly(vinyl chloride)

INTRODUCTION

Pheromones are behavior-modifying chemicals released by insects to communicate between members of the same species. Synthetic pheromones are being used widely because of their considerable potential in integrated pest management. The pheromone gossyplure,[1] a mixture of 1 : 1 Z,Z and Z,E isomers of 7,11-hexadecadienyl acetate (Fig. 1), is used for the control of the pink bollworm pest of the cotton crop. Efficacious use of pheromones depends on the availability of devices that could deliver them effectively at desired rates for the full crop period and also to protect them from degradation. Among the variety of such devices, blocks of PVC, rubber septa, plastic flakes, and trilaminate polymer films are successful examples.[2–4] Plasticized PVC membranes prepared by a solution-casting method are known to work as a highly versatile dispenser for the controlled release of pheromones.[5,6]

Knowledge of release kinetics plays a crucial role in the development of efficient formulations of dispensers, giving a rational delivery of pheromones. The concentration gradient at the interface and the release rates determined by convenient analytical techniques help in the design of dispenser formulations for controlled release. The relevance of release rates determined by any particular experimental method depends on the chemical or physical release mechanism and also

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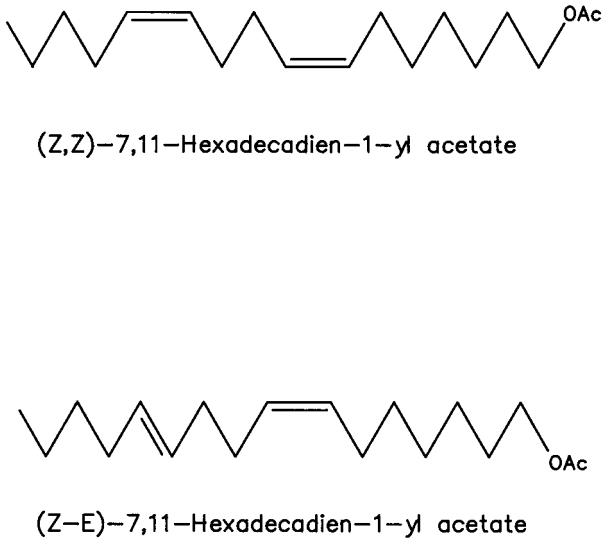

Figure 1 Chemical structure of two components of gossyplure.

on the medium for the release. The rates at which pheromones are emitted from a controlled-release formulation can be measured by three general methods: (i) collection of pheromone after release,[7,8] (ii) extraction of pheromone remaining in the formulation,[9,10] and (iii) measurement of the loss in weight of the dispenser after a definite period of exposure.[7] In general, measurement of pheromone release based on a weight-loss method is done[11,12] by hanging the devices in a temperature-controlled room and allowing diffusion to transport evaporated pheromone away from the formulation. In a case where analysis of the compound can be done by spectrophotometry, extraction of the formulation at intervals of release is followed.[13,14]

Several studies taking into consideration the methodology for measurement of emission rates and the effect of temperature on them and the relative performance of different apparatus based on chemical and biological evaluation were reported by Weisner and Silk.[15] In an effort to reduce the time required for each pheromone assay, thermal desorption from the collectors was suggested by Bierl-Leonhardt et al.[8] A laboratory procedure with sorbent tubes containing Tenax glass beads was developed by Leonhardt et al.[16] to measure the relative release rates of grandlure pheromone under conditions of constant temperature and air flow.

The design of suitable apparatus for the collection of pheromone released irrespective of the source is a critical requirement. Ideal apparatus are those wherein recovery of the emitted pheromone is quantitative under controlled conditions and there is absence of decomposition. Keeping these factors in view, an apparatus has been designed and fabricated for the estimation of the release rate of the pheromone from a PVC monolithic dispenser. The effect of the content of the plasticizer on the release rate of the pheromone was studied by using high-performance liquid chromatography (HPLC). Simultaneously, the release rate of the pheromone was also determined by the gravimetric desorption method, in order to asses the reliability of this method in comparison to the HPLC method for determining the diffusion coefficient of the pheromone.

EXPERIMENTAL

Materials

Commercial PVC (PR 124) supplied by Chemplast, Madras, India, having a weight-average molecular weight 1,90,375 and a number-average molecular weight of 97,600 (determined by the GPC); dimethyl phthalate (DMP), from Quality Products, Bombay; tetrahydrofuran (THF) and *n*-hexane of HPLC grade, from Ranbaxy, Bombay; and gossyplure pheromone of 99% purity, a product of Pheromones India, Bapatla, were used.

Membrane Preparation

PVC membranes of uniform thickness, 150 ± 2.5 μm plasticized with DMP (10, 17.5, and 22.5% by weight) and loaded with gossyplure (1.5 mg/cm^2) were prepared using a solution-casting method.[5,6,17] A 6% (by weight) solution in THF containing calculated amounts of PVC, DMP, and gossyplure was poured over a clean mercury surface in a nonsticking bath and left overnight in a chamber for the solvent to evaporate. The dried film/dispenser was gently removed from the mercury bath and cleaned with a camel's-hair brush. The edges of the film which were in contact with the walls of the bath were cut. A portion of the film of uniform thickness (150 ± 2.5 μm) was selected for determining the release rate of pheromone from it.

Determination of Release Rates

The rate of emission of pheromone from the film (a dispenser loaded with 1.5 mg/cm^2 pheromone) was

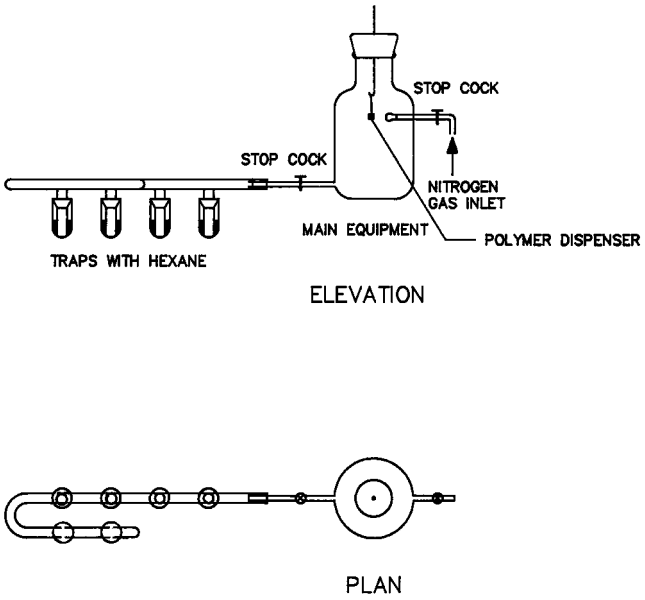

Figure 2 Schematic diagram of solvent trap assembly for the collection of pheromone released.

measured in a room conditioned at 25 ± 1°C by using the apparatus described in Figure 2. Six glass tubes, each containing 10 mL of HPLC-grade *n*-hexane, were connected to the U-shaped glass assembly housed in a thermostatically controlled chamber maintained at 0 ± 1°C. One of the ends of the assembly was connected to the fused glass jar in which a 4 × 4 cm piece of the dispenser was hung in the center opposite to the inlet for dry N_2 gas flow at a rate of 100 mL/min and the other end is left open for the exit of N_2. The pheromone along with N_2 gas was allowed to bubble through tubes containing *n*-hexane to trap the pheromone released from the dispenser. The set of tubes containing *n*-hexane was replaced by a fresh set of tubes at an increasing interval of 12, 16, and 24 h to estimate the emission of pheromone with time. No amount of pheromone could be detected in the sample from the sixth tube and only traces of it was found in the content of the fifth tube. At the end of the experiment, the U-shaped glass assembly and glass jar were rinsed with *n*-hexane for estimation of the pheromone adsorbed on their surface. The experiments were done in triplicate and the mean results are reported. Reproducibility was found to be within 2% of the mean.

Calibration Plot of the Standard Gossyplure Solutions

A series of working calibration solutions ranging from 50 to 500 μg/L were prepared by appropriate dilution of a 500 μg/L stock solution. A 20 μL aliquot of the solution was injected into the HPLC unit. The peak areas obtained from the chromatograms were plotted against the corresponding concentrations and used as a calibration plot. The concentration of the pheromone in the sample was identified by comparison of its retention time with that of the calibration standard.

Estimation of the Pheromone Content by HPLC

The amount of the released pheromone, gossyplure, trapped in the solvent samples was determined by an HPLC (Model LC 6A, Shimadzu Corp., Japan) equipped with a 6A, Shimadzu UV-visible spectrophotometer. A 20.0 μL aliquot of each sample at 1.28 μ sensitivity of the UV detectors was injected onto a silica column of 4.6 × 25 mm attached to a Shimadzu guard column of 4.6 × 60 mm. A mobile phase of *n*-hexane with a flow rate of 1 mL/min at a pressure of 62 kg/cm^2 was used. The chromatograms obtained had a single retention time of 3.72 for the two components of the gossyplure pheromone and were detected by UV absorption at 270 nm. The area of the peak for each sample was compared with the calibration curve of standard solutions of gossyplure. The initial loading of gossyplure in the fresh dispenser and the residual amount of gossyplure in the aged dispenser was estimated by solvent extraction in *n*-hexane.

RESULTS AND DISCUSSION

In the course of diffusion, the pheromone molecule reorients several segments of the polymer chains in the membrane in order to migrate. The presence of a codiffusant or plasticizer as an additive may influence the segmental arrangement of the polymer chains in the membrane by softening or plasticizing the polymer matrix. The concentration of the plasticizer in the dispenser plays a pivotal role by altering the emission rates of the pheromone and the performance of the dispenser.[18,19]

Emission Rate of Gossyplure by HPLC Method

The experiments were conducted on the 150 ± 2.5 μm-thick PVC dispensers (plasticized with 10, 17.5, or 22.5% of DMP) of a 16 cm^2 area loaded with 24 mg of gossyplure. The average emission

Table I Emission Rates of Gossyplure from Plasticized PVC Dispensers

Concn of DMP in the Dispenser (%)	Initial Loading Gossyplure (mg)	Emission Rate $\times 10^2$ (mg/h)			Residual Amount Gossyplure After 30 Days (mg)
		t_1	t_2	t_3	
10.0	21.99	0.66	0.40	0.35	18.09
17.5	21.86	0.95	0.55	0.46	17.08
22.5	21.93	1.23	0.75	0.68	16.21

t_1 = the average emission rate during first 12 h; t_2 = the average emission rate after next 12 h; t_3 = the average mission rate after next 30 days.

rates reported in Table I are found to increase with increasing DMP concentration. This could be due mainly to the increase in free volume of the polymer membrane and increased polymer chain segmental mobility.

During the first 12 h, the emission rate per hour, t_1, was found to be more due to the initial burst, which later becomes almost steady, t_2, obeying Fick's laws of diffusion. The dispensers were aged indoor for a period of 30 days and their emission rate, t_3, was estimated. The insignificant difference between t_2 and t_3 indicates the effective functioning of the dispenser as a controlled-release device for the emission of pheromone even after 30 days. The initial loading of the pheromone in the fresh dispenser and the residual amount in the aged dispenser were estimated from the solvent extract obtained on soaking the membrane in *n*-hexane for 24 h. No evidence of the decomposition of gossyplure was observed in the chromatograms of the aged dispensers. The residual amount of gossyplure present in the aged dispenser indicates that it contains a sufficient amount of the gossyplure and ensures its effectivity even after 30 days of exposure.

Diffusion Coefficient

The nonporous, homogeneous polymer membranes used for dispensing pheromone are usually known as solution–diffusion membranes. The mechanism of release of the pheromone through a membrane material which does not have any pores is mainly by absorption, solution, and diffusion down the gradient of thermodynamic activity and final desorption.[3,18] The release process is governed mainly by Fick's law of diffusion.[20]

In diffusion kinetic studies, the release of a desorbing molecule (in this case, pheromone) is recorded as a function of time under controlled experimental conditions. The amount released according to Fick's law of diffusion is plotted in terms of M_t/M_∞ vs. $\sqrt{t}$ and the plot is linear during the initial stages:

$$M_t/M_\infty = 4/l(Dt/\pi)^{1/2} \quad (1)$$

where M_t and M_∞ are the cumulative masses of pheromone (gossyplure) desorbed from the membrane at time t and at t_∞ (in this case, t_∞ is 30 days). The thickness of the dispenser is l and D is the diffusion coefficient of pheromone.

The diffusion characteristics of pheromone dispersed in the polymer matrix provide useful infor-

Table II Data on Diffusion of Gossyplure from PVC Dispensers Determined by HPLC Method

Concn of DMP in the Dispenser (%)	$\sqrt{t}$ $(s)^{1/2}$	M_t/M_∞	Slope (θ) $\times 10^4$ ($s^{-1/2}$)	Diffusion Coefficient $D \times 10^{13}$ (cm^2/s)
10.0	85	0.0072	0.97	4.12
	120	0.0117		
	170	0.0164		
	208	0.0202		
	300	0.0291		
17.5	85	0.0089	1.12	5.59
	120	0.0135		
	170	0.0186		
	208	0.0234		
	300	0.0337		
22.5	85	0.0116	1.30	7.47
	120	0.0152		
	170	0.0225		
	208	0.0259		
	300	0.0374		

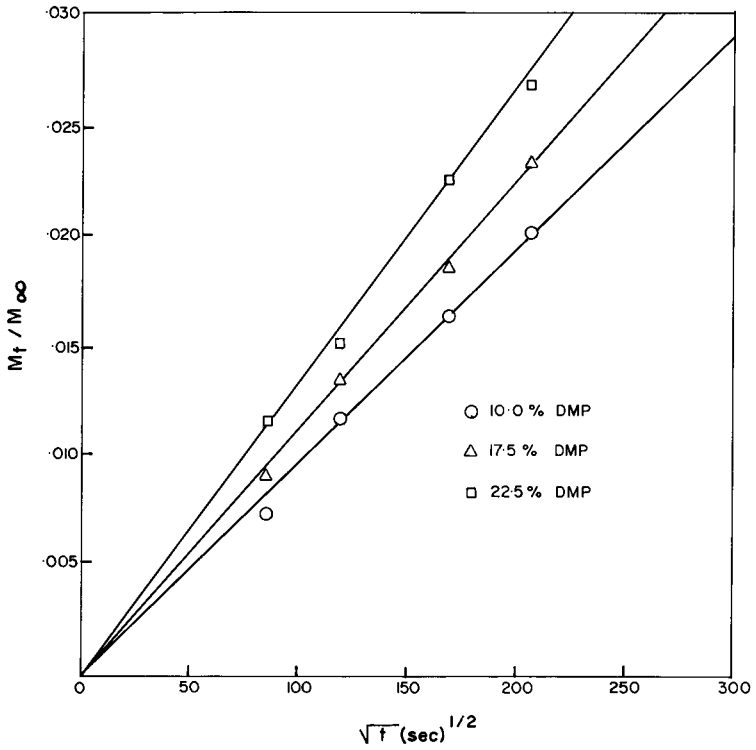

Figure 3 Release of gosyplure from plasticized PVC membranes (HPLC method).

mation for the design of controlled-release formulations. The presence of a certain amount of plasticizer in the PVC membrane increases the free volume in the polymer matrix, which, in turn, promotes diffusion of the active ingredient. The plasticizer is often referred to as releasing agent, as it dissolves the pheromone and helps its transport to the surface of the dispenser. The data of the release rate of pheromone (gossyplure) through PVC dispensers are reported in Table II.

The plots of M_t/M_∞ vs. $\sqrt{t}$ in Figure 3 are in accordance with Fick's law of diffusion. The coefficient of diffusion, D, of the dispenser for gossyplure was derived by substituting the slope of the plot in eq. (1). The increase in the diffusion coefficient is found to be directly proportional to the concentration of DMP in the dispenser.

The technique described here is expected to produce reliable information about the release of a pheromone or of any other relatively volatile active ingredient dispersed in a polymer matrix. Data generated by this study with respect to specific parameters can be used in designing the effective formulations for the release of a dispersed active ingredient at the desired rate for a specific period. In this study, the experimental conditions are to be followed rigidly for better reproducibility of the data. The solvents required are of HPLC grade and the experiment can be conducted on one specimen at a time. The experiment conditions described in this technique are good for the reproducibility of the results, but they do not simulate the field conditions.

Emission Rate of Gossyplure by Gravimetric Desorption Method

By taking the various aspects described above into consideration, a set of experiments using a simple experimental technique based on gravimetric estimation of desorption of pheromone by recording the weight loss of the dispenser with time was conducted. The diffusion kinetics data obtained from the gravimetric desorption method were compared with those obtained from the estimation of the desorbed pheromone by the HPLC technique.

Polymer dispensers with or without pheromone (blank) were prepared as per the method described earlier and selected membranes of uniform thickness were used for the experiments. Plasticized PVC membranes without pheromone

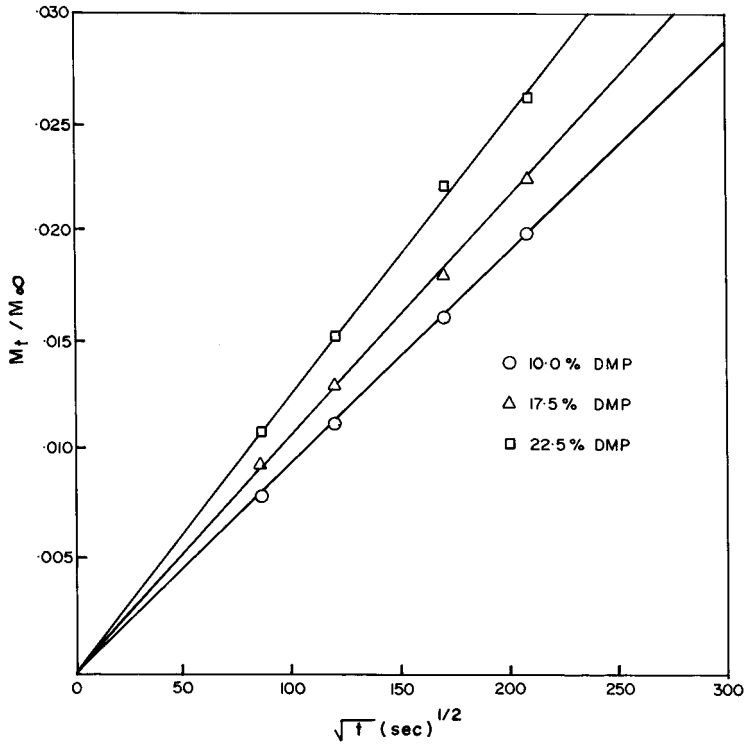

Figure 4 Release of gossyplure from plasticized PVC membranes (gravimetric desorption method).

as well as the corresponding membranes loaded with gossyplure pheromone were hung in a room conditioned at 25 ± 1°C with air circulation to transport evaporated pheromone away from the dispenser.

The solvent and the pheromone evaporate simultaneously from the dispenser prepared by solution casting. Therefore, simultaneously, the weight loss of the membranes loaded with pheromone and those containing no pheromone was recorded as a function of time to account for the decrease in weight due to loss of solvent and due to the quantity of solvent and pheromone released from the membrane. The time interval of weight loss recording was 1 h on the first day, which was later increased to 2, 4, 8, 24 h and then weekly.

At a particular time interval, t, the amount of pheromone released from the membrane is denoted as M_t and the loss in the weight of the membrane due to evaporation of the solvent is denoted by M_{ts}. M_{tsp} denotes the combined weight of pheromone and the solvent diffused from the membrane. The amount of pheromone released, M_t at time t and M_∞ at t_∞ (120 days), was calculated by using the following relationships:

$$M_t = M_{tsp} - M_{ts} \quad (2)$$

$$M_\infty = M_{\infty sp} - M_{\infty s} \quad (3)$$

where $M_{\infty sp}$ is the total amount of solvent and pheromone diffused from the pheromone-loaded dispenser and $M_{\infty s}$ is the amount of solvent diffused from the PVC membrane (blank). Here, the t_∞ = 4 months, which is taken on the basis of the crop period beyond which the pheromone-loaded polymer dispensers are not used in the agriculture field.

The values of M_{t1}/M_∞, M_{t2}/M_∞ $\cdots$ were plotted against $\sqrt{t_1}$, $\sqrt{t_2}$ $\cdots$ and the value of the diffusion coefficient, D, for gossyplure diffused from each formulation was calculated by using the corresponding slope, θ, obtained from the plots (Fig. 4). A part of the data obtained from this study is reported in Table III.

In the case of the gravimetric desorption method, the pheromone loaded in the membrane

Table III Data on Diffusion of Gossyplure from PVC Dispensers Determined by Gravimetric Desorption Method

Concn of DMP (%)	$\sqrt{t}$ $(s)^{1/2}$	M_t/M_∞	Slope $\times 10^4$ (θ) $(s^{-1/2})$	$D \times 10^{13}$ (cm^2/s)
10.0	85	0.0076	0.57	3.98
	120	0.0112		
	170	0.0160		
	208	0.0198		
	300	0.0286		
17.5	85	0.0091	1.06	5.04
	120	0.0130		
	170	0.0179		
	208	0.0224		
	300	0.0323		
22.5	85	0.0108	1.26	7.03
	120	0.0152		
	170	0.0221		
	208	0.0263		
	300	0.0379		

releases simultaneously along with the solvent used for casting the film. To obtain reproducible results, care was taken in the maintenance of the experimental conditions such as temperature, humidity, and air circulation in the room where the polymer dispensers were hung. The experiments were done simultaneously in quadripulate for each measurement, and the reproducibility of the data was within 5% of the mean.

The diffusion coefficient data of pheromone reported in Tables II and III indicates that the D values obtained by the gravimetric desorption method are slightly lower (D = 3.98, 5.04, and 7.03×10^{-13} cm^2/s) in comparison to those obtained by HPLC analysis (D = 4.12, 5.59, and 7.47×10^{-13} cm^2/s) for the PVC membranes plasticized with 10.0, 17.5, and 22.5% DMP, respectively. The release rate and the diffusion coefficients of the pheromone obtained from the HPLC method under precisely controlled experimental conditions and the data obtained from gravimetric desorption method, with less rigid experimental conditions, were found to be reasonably comparable to each other.

CONCLUSIONS

The morphology of the polymer membrane controls the emission rate of pheromones. The concentration of the codiffusant/plasticizer can alter the energy of free rotations, free volume, and intermolecular attractions of the polymer membrane and, consequently, the release rate of pheromone.

The simple technique of gravimetric desorption can provide reliable information about the release rate of pheromone from a dispenser and help in the prediction of its performance in integrated pest management. This method was found to be economical and practical and allows a simultaneous estimation of a large number of samples.

The controlled-release device thus developed worked effectively for more than 30 days as indicated by the presence of a large amount of residual pheromone in the aged dispenser. No indication of degradation of the pheromone was observed in the chromatograms of the aged dispensers. The release kinetic studies provide useful information in the design of controlled-release formulations.

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